

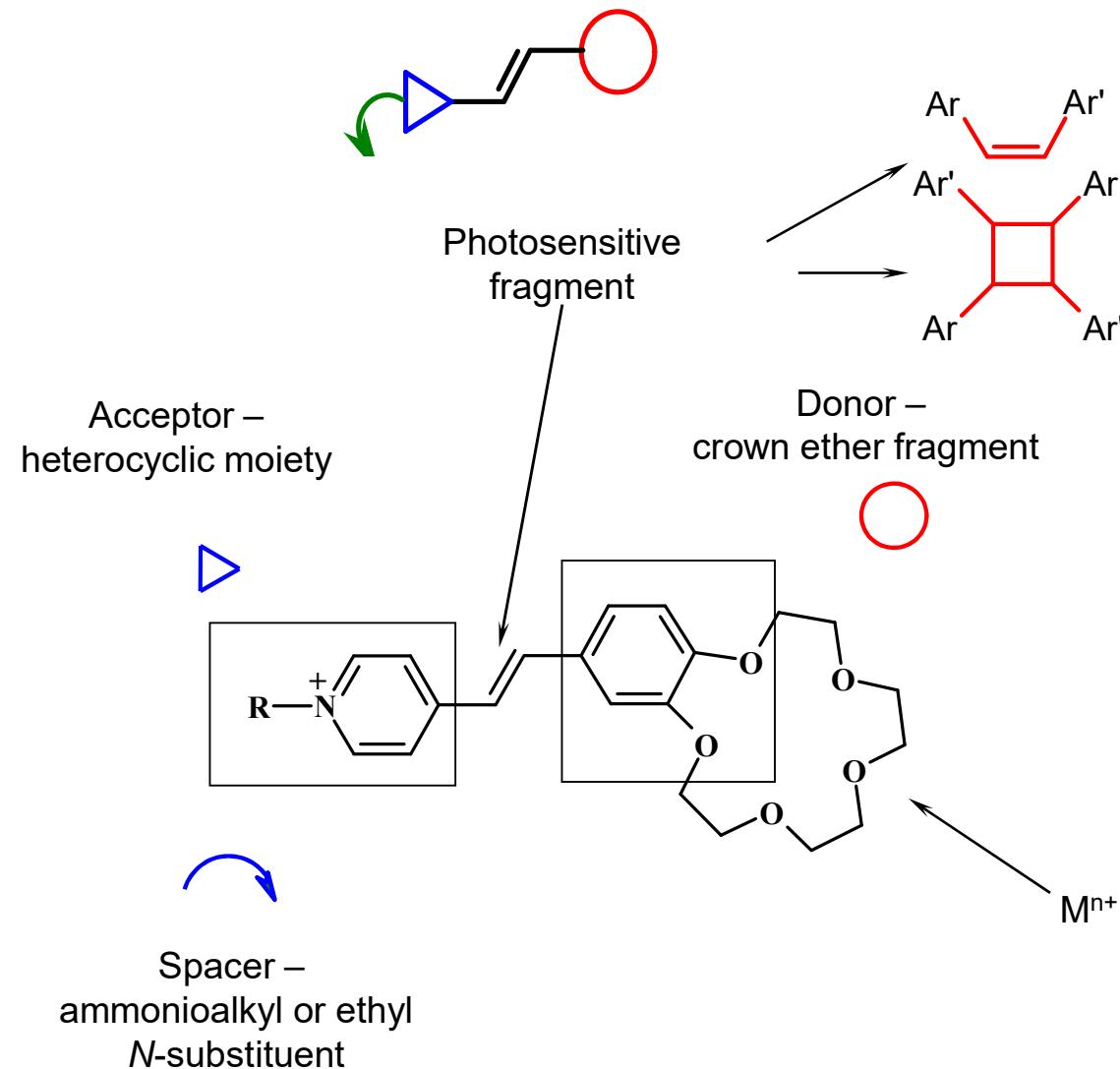


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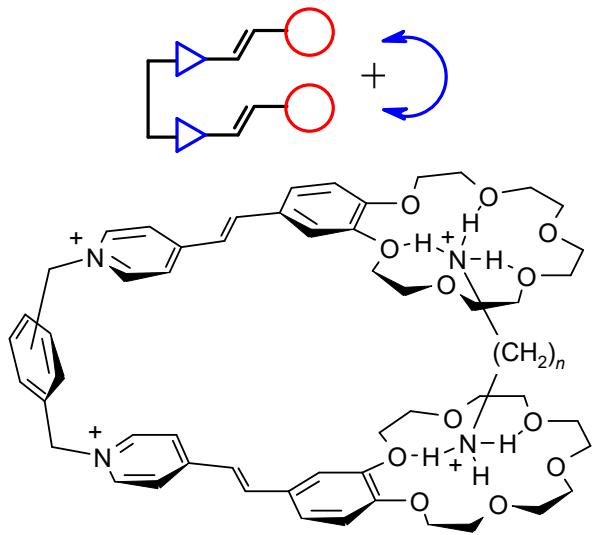
**CROWN-CONTAINING STYRYL DYES WITH AMMONIOALKYL
SUBSTITUENTS: DIMERIZATION AND STEREOSPECIFIC
[2+2]-PHOTOCYCLOADDITION**

*N. A. Lobova, A. I. Vedernikov, S. N. Dmitrieva, E. N. Ushakov,
L. G. Kuz'mina, M. V. Alfimov, S. P. Gromov*

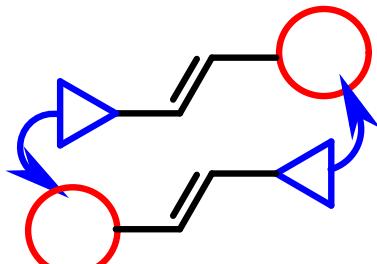
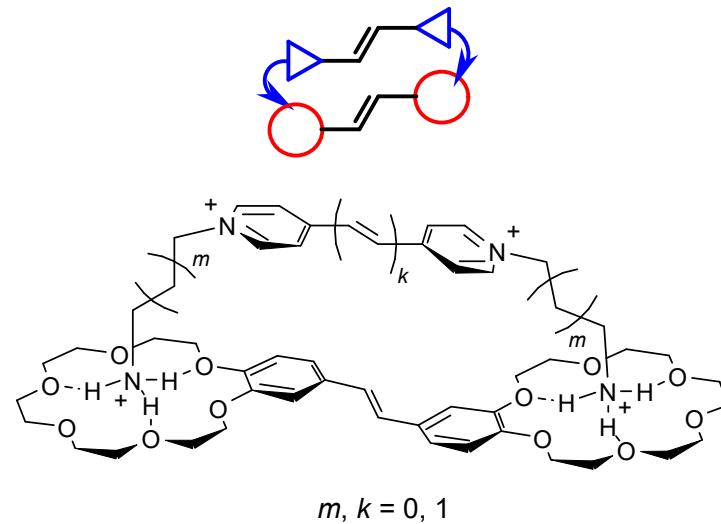
Principles of photosensitive supramolecular systems invention



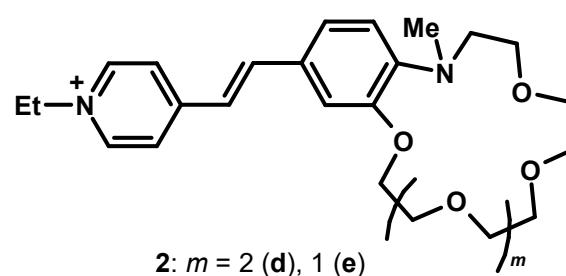
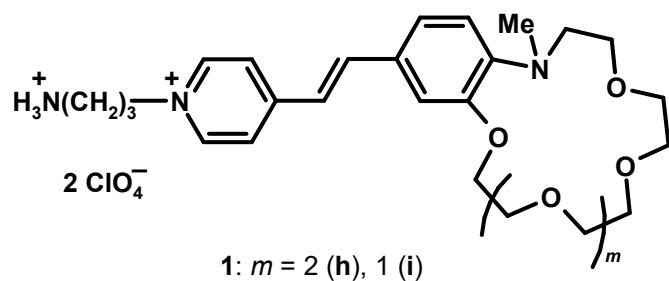
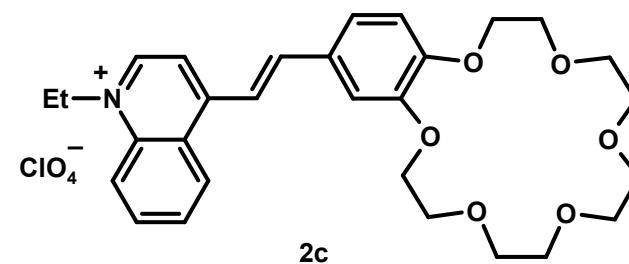
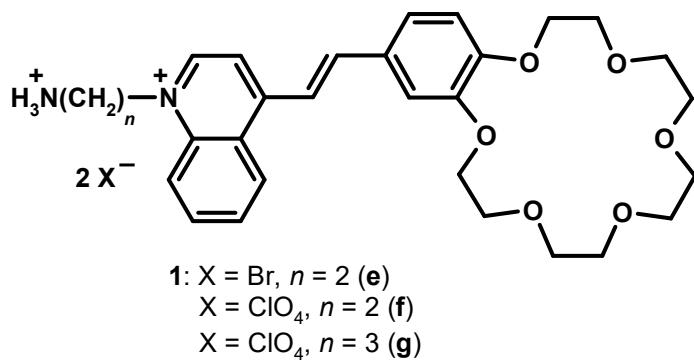
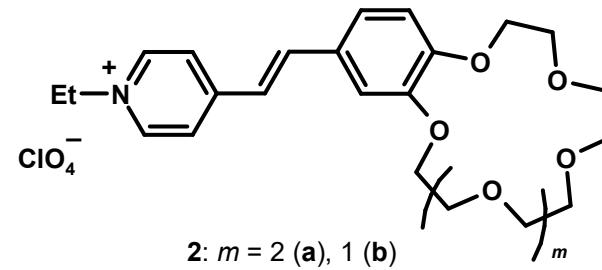
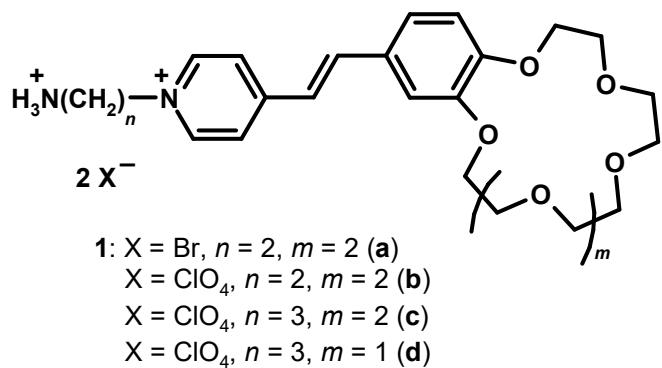
Types of supramolecular systems



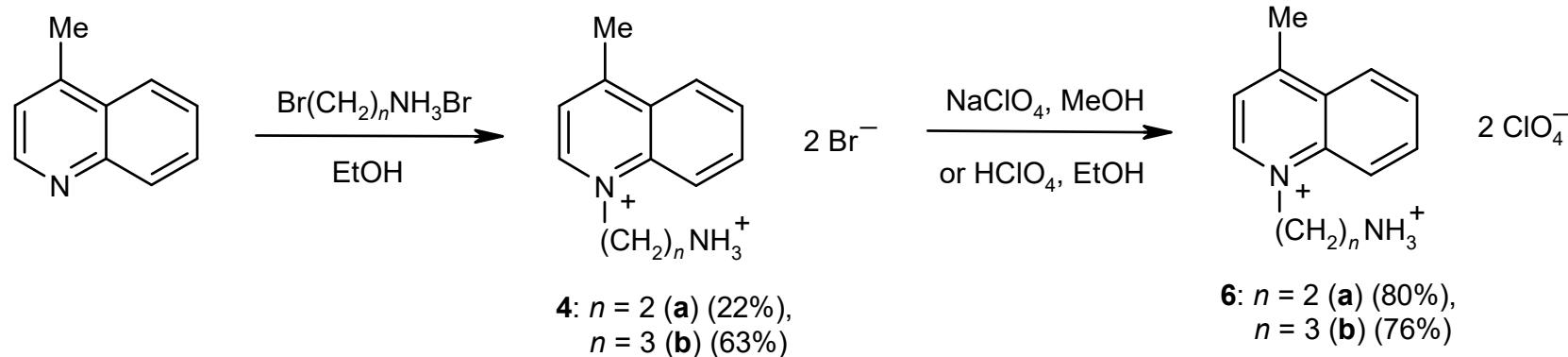
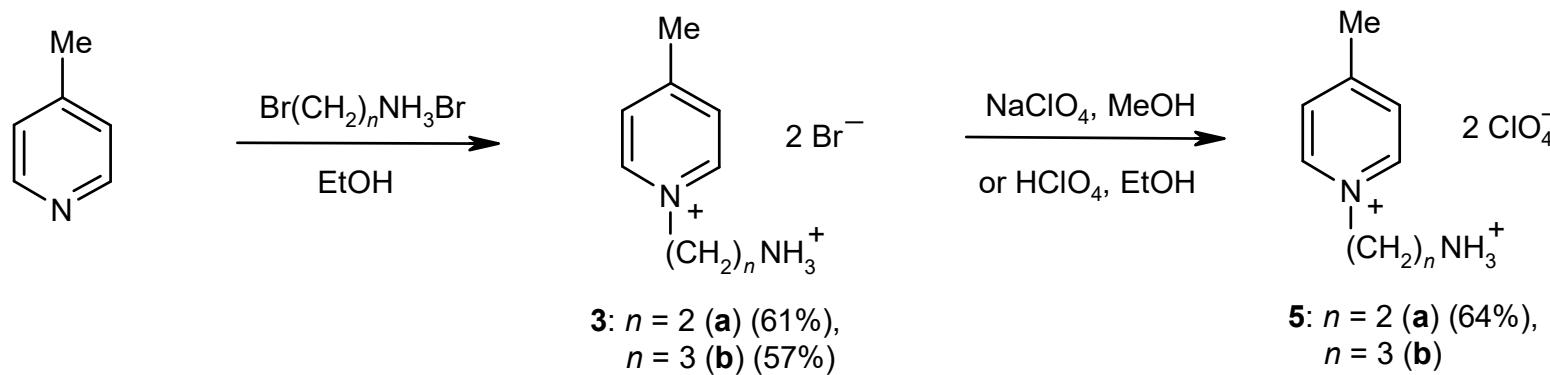
Patent RF № 2389745. – 2010. - № 14.



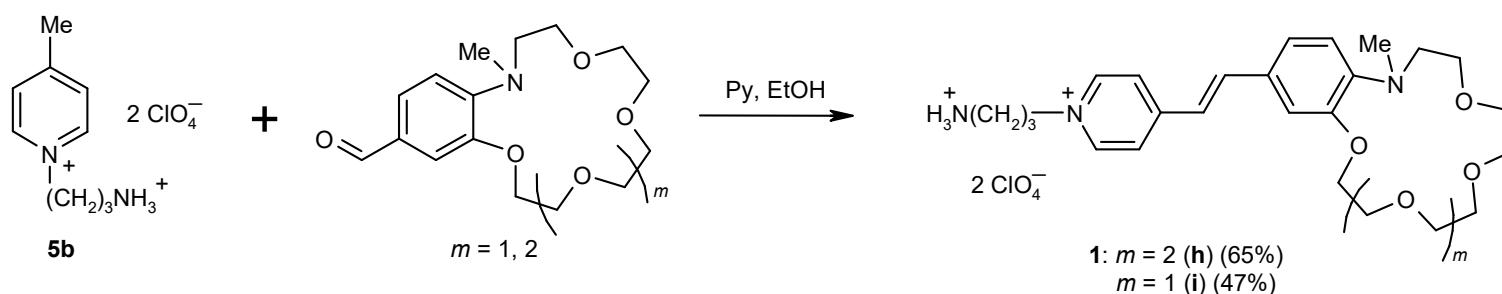
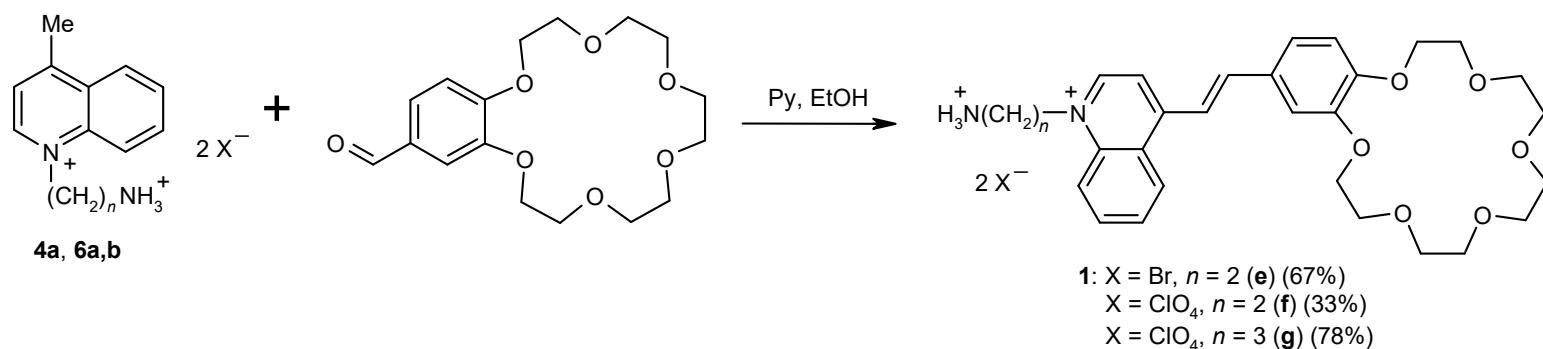
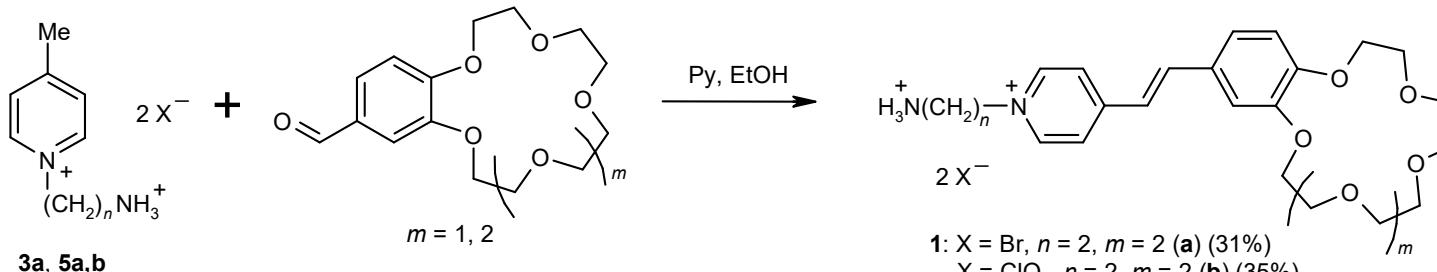
Investigated styryl dyes



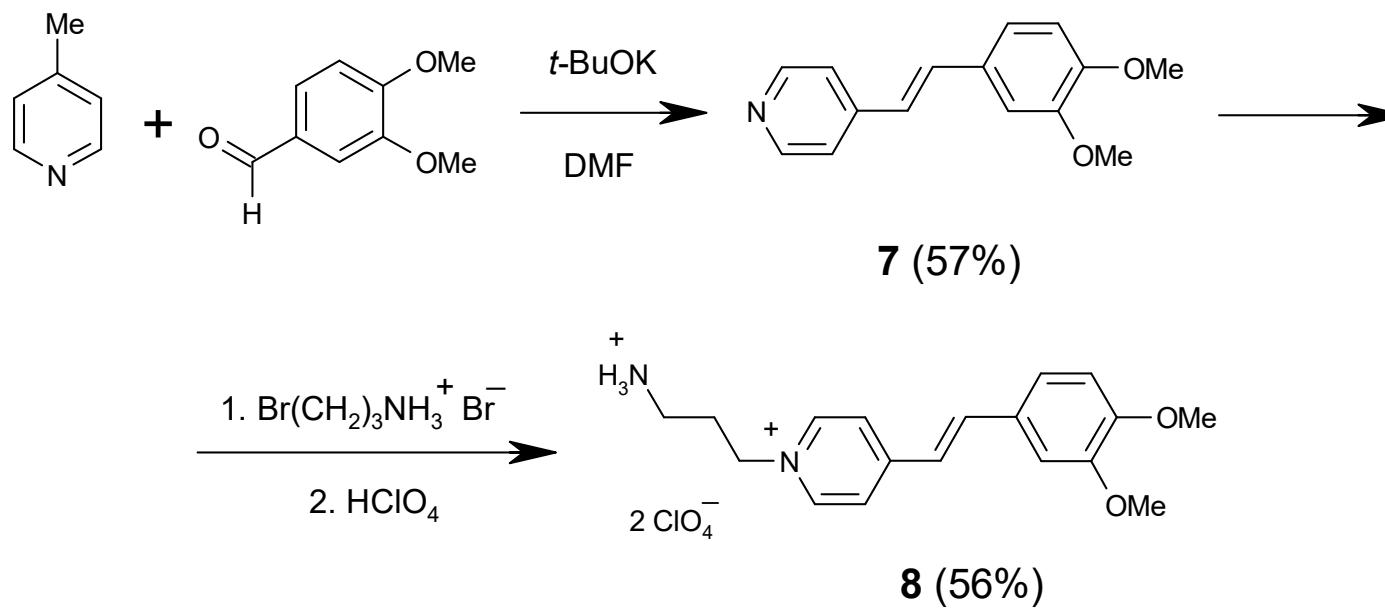
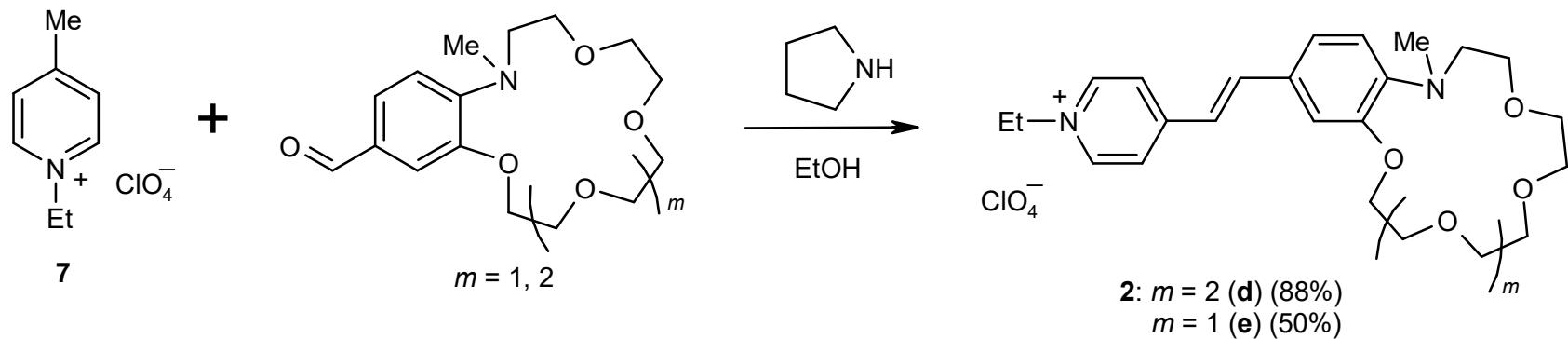
Synthesis of quaternary salts



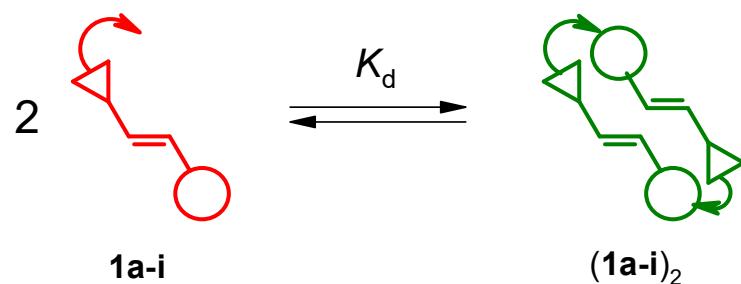
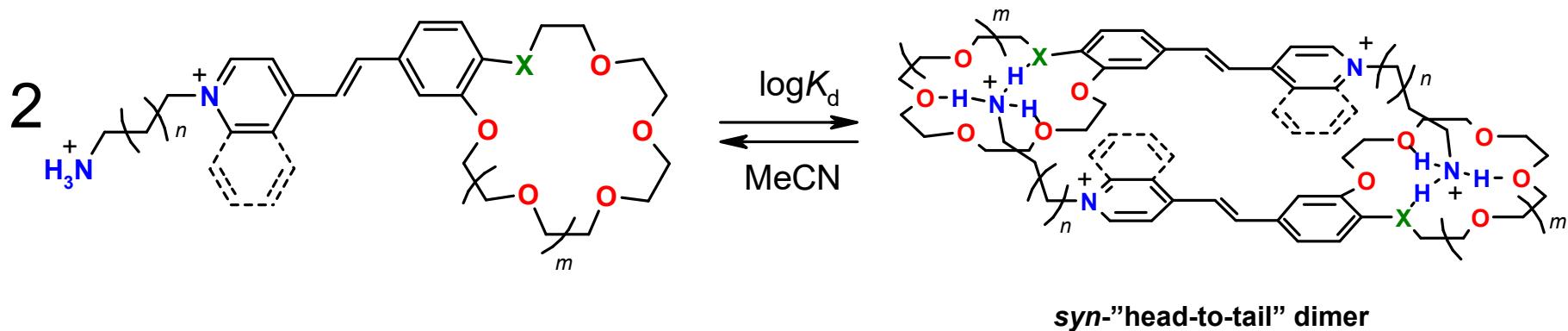
Synthesis of styryl dyes



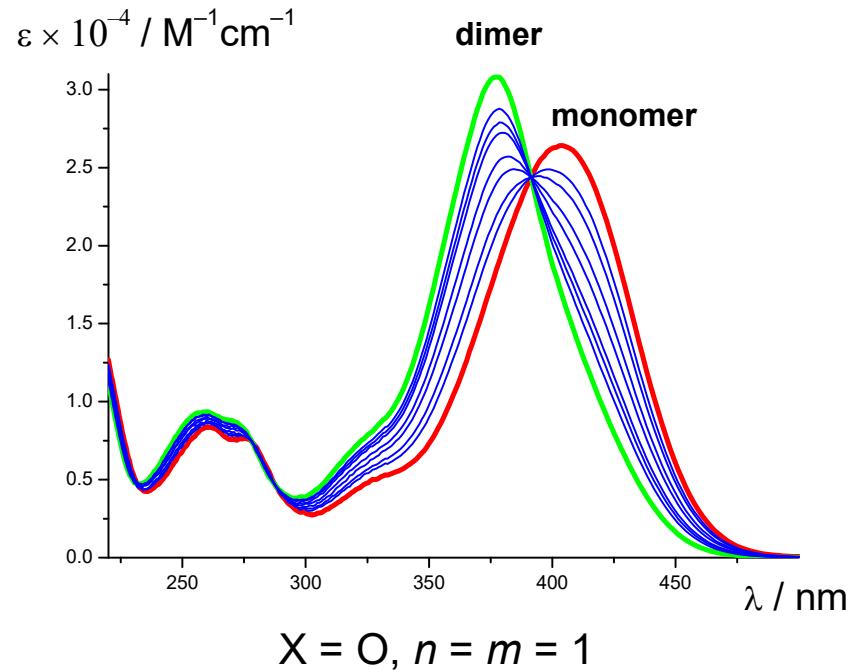
Synthesis of reference styryl dyes



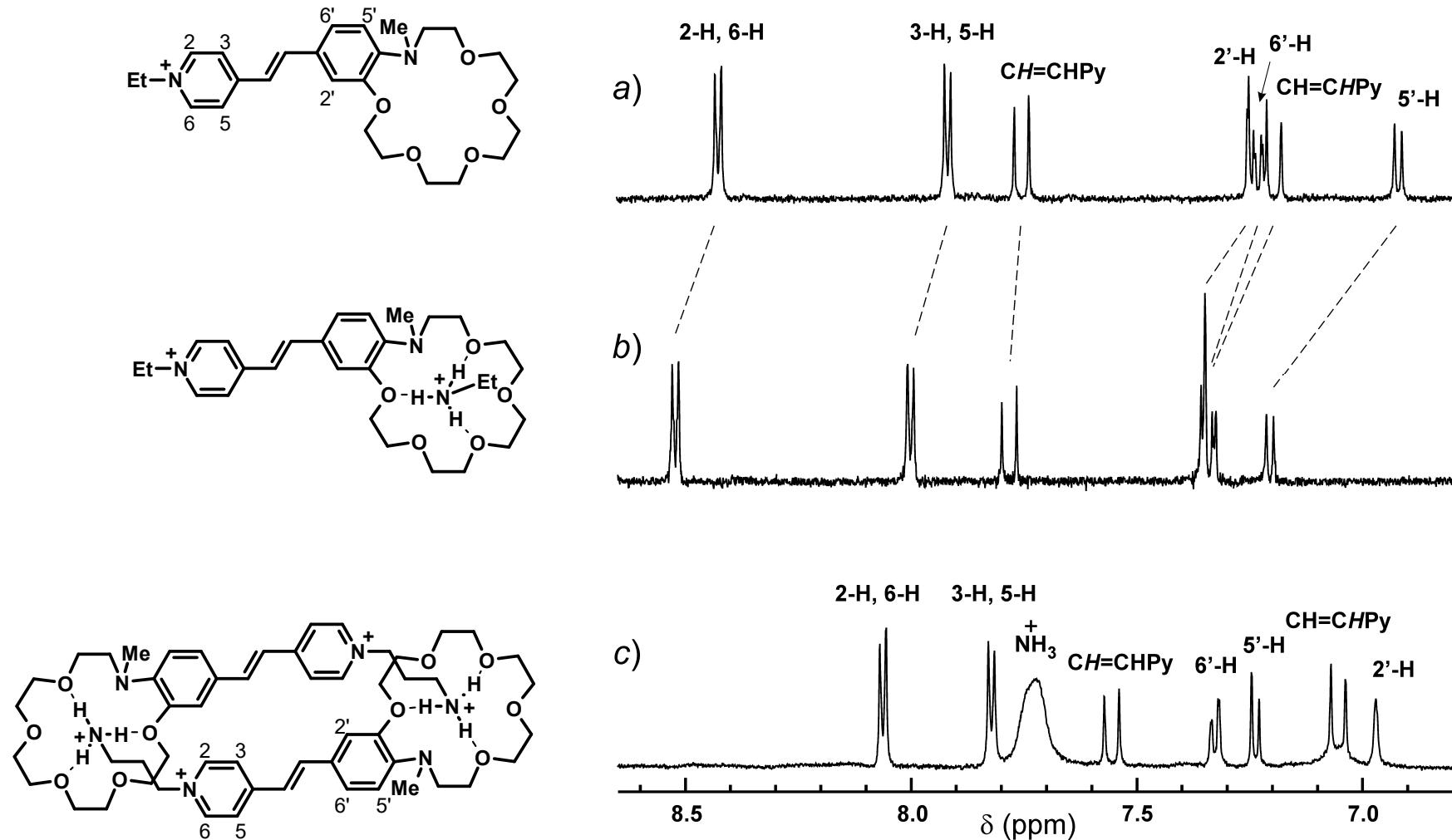
The formation of styryl dye dimers



Concentration dependence of absorption spectra
for dye **1c** in water-acetonitrile mixture
and calculated spectra of dimer and monomer



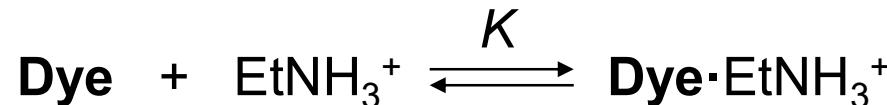
The dimerization of styryl dyes



^1H NMR spectra in $\text{MeCN}-d_3$.

The stability of reference crown-containing styryl dyes with $\text{EtNH}_3^+\text{ClO}_4^-$

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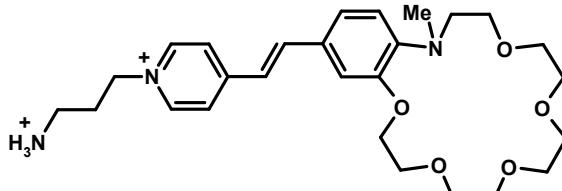
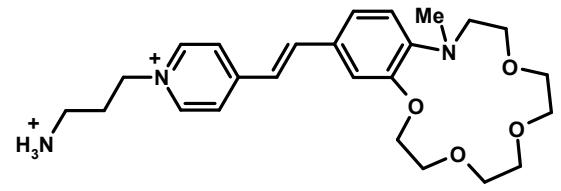
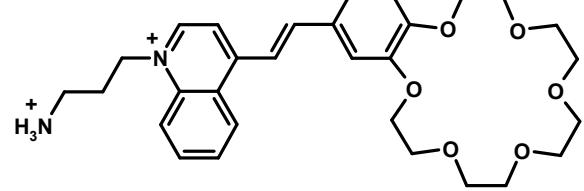
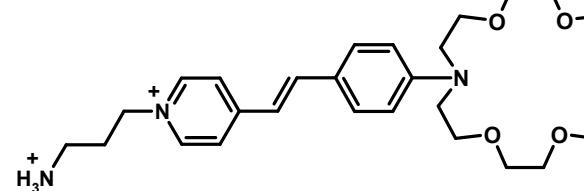
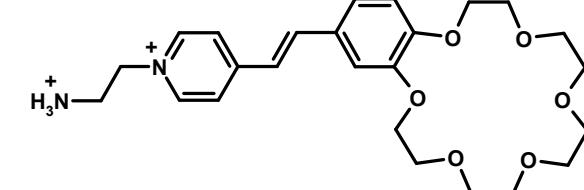
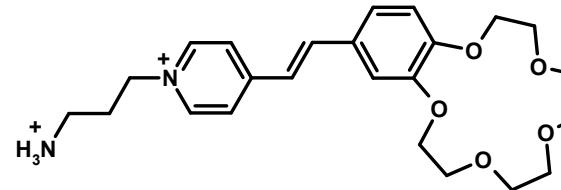
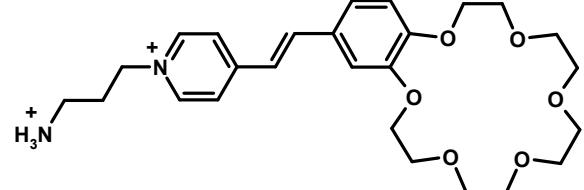


Dye	$\log K^{\text{ef}}$	Dye	$\log K^{\text{ef}}$
	3.9		1.9
	3.6		1.8
	3.5		

in $\text{MeCN}-d_3$

from NMR titration data

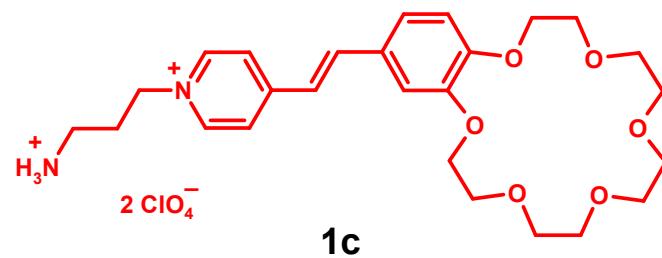
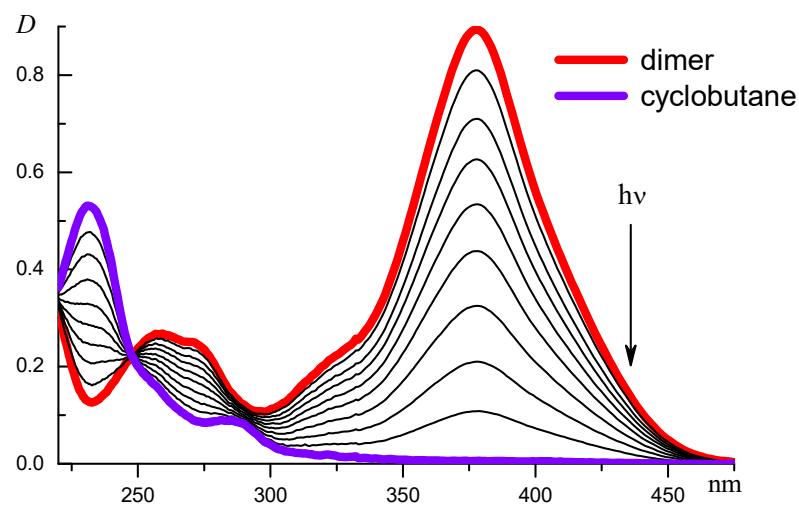
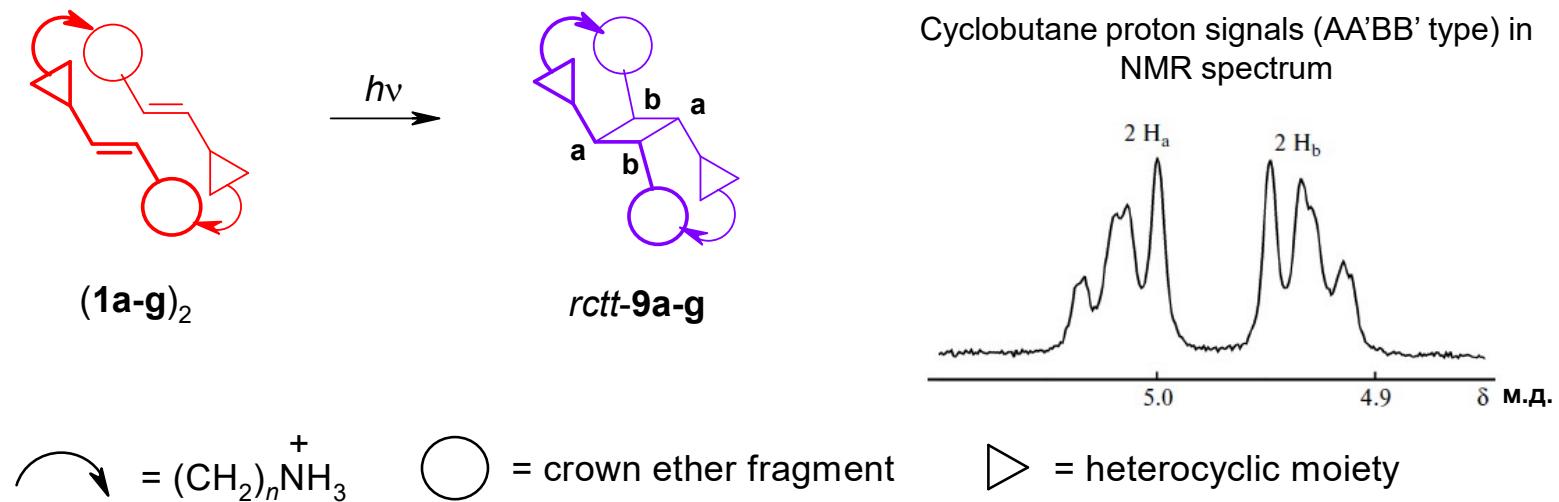
The stability of ammonioalkyl styryl dye dimers

Dye	$\log K_d^{\text{ef}}$	Dye	$\log K_d^{\text{ef}}$
	8.2 (8.8)		3.6 (3.7)
	8.0 (7.7)		3.6 (3.6)
	7.9 (8.1)		2.4 (3.5)
	7.1 (7.3)		

in MeCN-*d*₃

from competitive NMR (UV) titration data

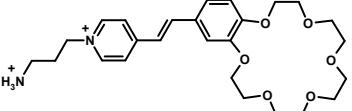
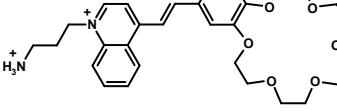
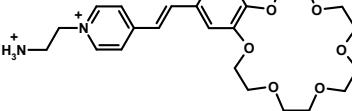
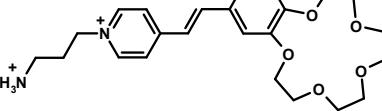
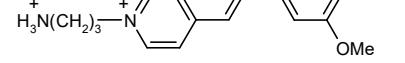
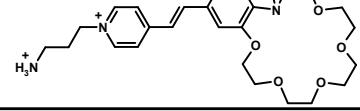
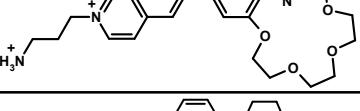
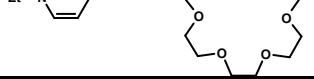
[2+2]-photocycloaddition in dimers



Irradiation of dye **1c** solution in MeCN.

JOC., 2014, 79, 11416 -11430

The reaction effectiveness of cyclobutane formation

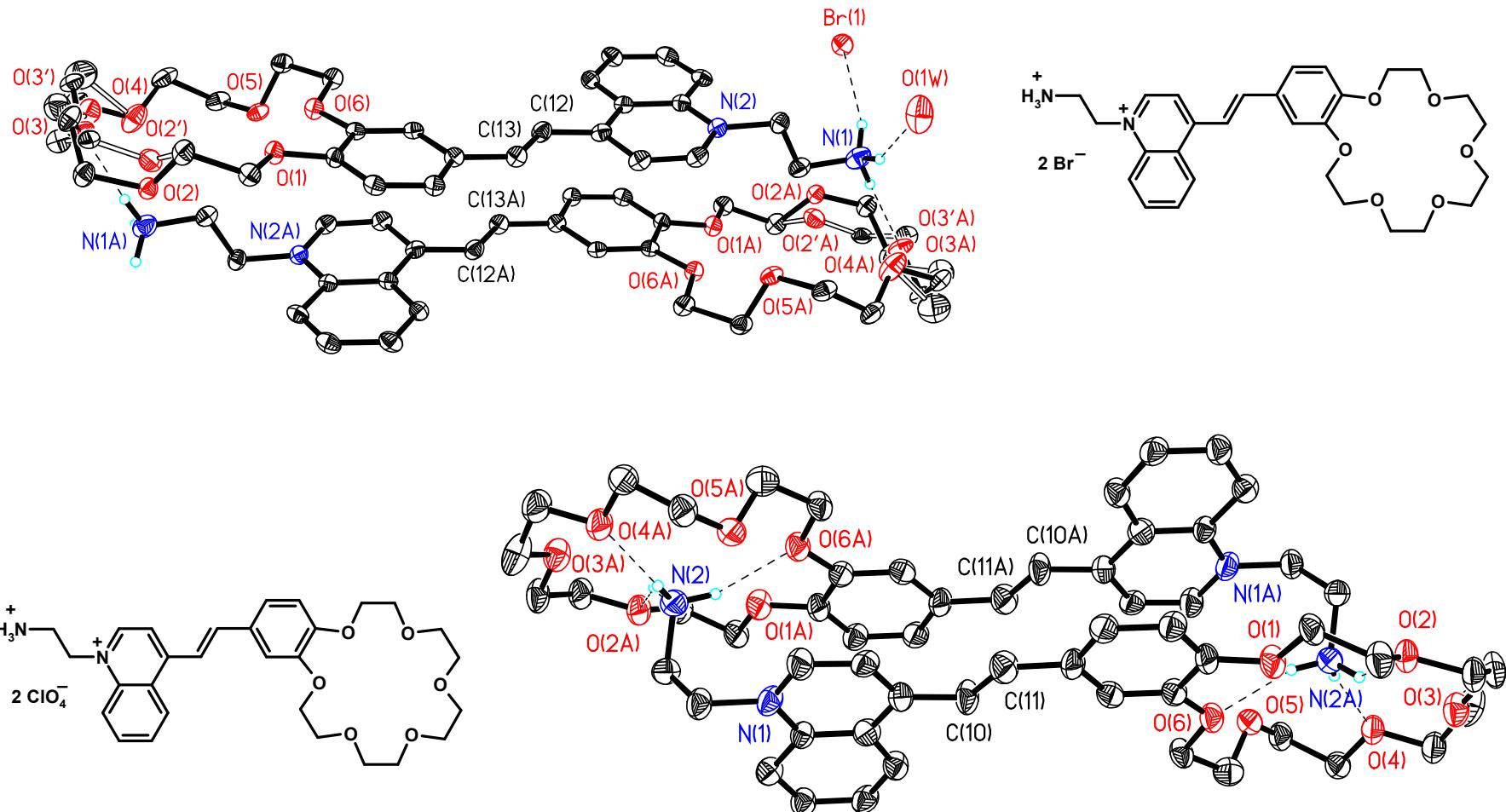
Dye	Irradiation time, h	Degree of conversion, %
	4	100
	4	100
	4	40
	20	100
	4	33
	20	100
	30	< 1
	40	0
	40	0
	30	0

Quantum yields of the reaction of [2 + 2] -photocycloaddition of supramolecular dimers of ammonioalkyl styryl dyes and key characteristics of cycloproducts

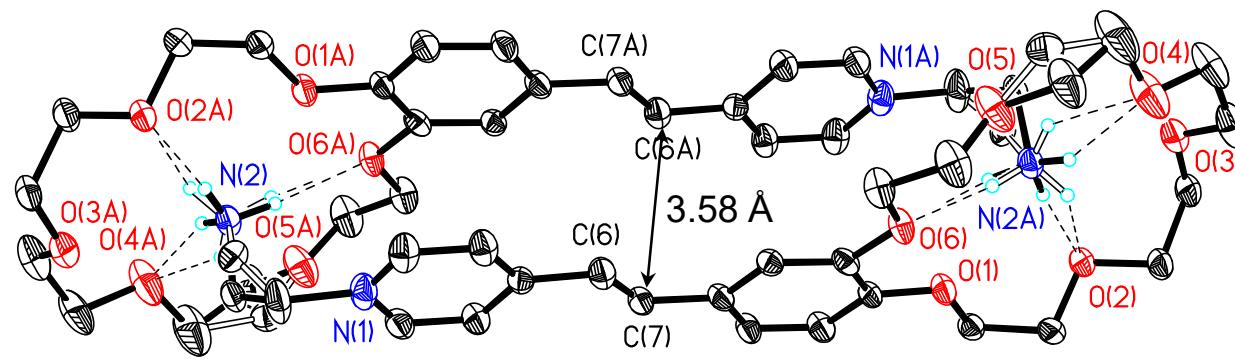
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B MeCN		Cycloproducts		
Dye dimer	$\Phi_{[2+2]}$	λ_{\max} , HM	$\varepsilon \cdot 10^{-4}, M^{-1} \cdot cm^{-1}$	
	0.38	286	0.62	
	0.049	288	0.64	
	0.26	286	0.58	
	0.27	319	1.38	
	0.0065	321	1.14	

Dimeric organization of styryl dye cations

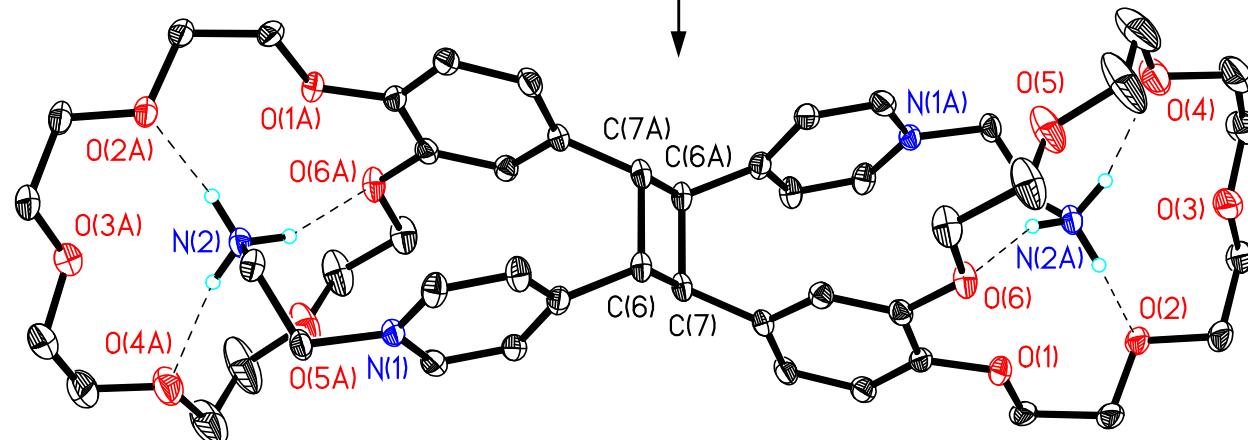


“Single crystal – to – single crystal” photoreaction

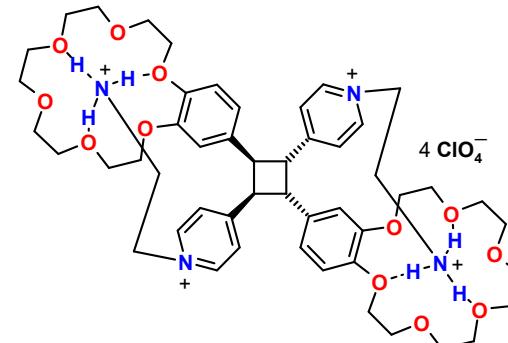
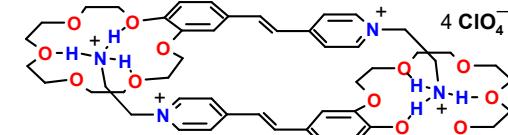


syn-«head-to-tail» dimeric pair

$h\nu$



rctt-cyclobutane



CONCLUSIONS:

- A broad series of ammonioalkyl styryl dyes were synthesized
- Their ability to form stable pseudocyclic dimer ($\log K_d$ is up to 8.8) in solution, in solid phase and in crystals was investigated
- Dimers are pre-organized to stereospecific [2+2]-photocycloaddition
- The only *rctt* isomer of cyclobutane derivative forms as a result of the photoreaction
- The quantum yield of [2+2]-photocycloaddition is up to 0.38
- Photocycloaddition in crystal occurs without crystal degradation
- We believe that such structures can be employed in the systems of optical information storage

*Thank you for your
attention!*