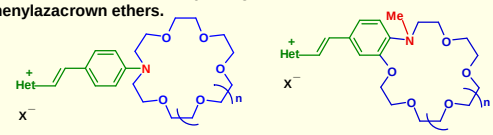
Synthesis, structure, and properties of novel chromo(fluoro)ionophores based on *N*-methylazacrown-ether styryl dyes

РОССИЙСКАЯ АКАДЕМИЯ НАУК
ЦЕНТР ФОТОХИМИИ

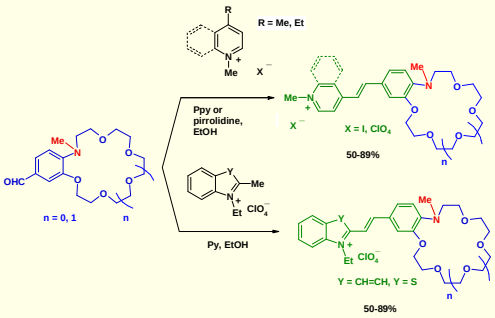
Dmitrieva S.N.,[1] Ushakov E.N.,[1,2] Vedernikov A.I.,[1] Kurchavov N.A.,[1] Kuz'mina L.G.,[3] Sazonov S.K.,[1] Alfimov M.V.,[1] Gromov S.P.[1]

[1] *Photochemistry Center of the RAS, Moscow, Russia*
[2] *Institute of Problems of Chemical Physics of the RAS, Chernogolovka, Russia*
[3] *N. S. Kurnakov Institute of General and Inorganic Chemistry of the RAS, Moscow, Russia*

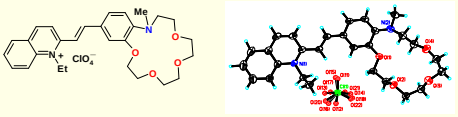
INTRODUCTION Currently a topical problem is the development of selective and sensitive sensors for analytical applications in chemistry, biology, medicine, ecology, and other fields. In this connection, of considerable interest are chromogenic and luminogenic crown compounds (chromo- and fluoroionophores) able to change their photophysical properties considerably upon selective binding of a substrate. They are expected to find use in portable optical devices for determination of metal cations and some organic cations. The design of intrinsic chromo(fluoro)ionophores based on electron-coupled donor-acceptor systems often makes use of *N*-phenylazacrown-ether moieties, as they have good electron-donating properties. A substantial drawback of the chromogenic *N*-phenylazacrown ethers is low thermodynamic stability of the complexes with alkali and alkaline-earth metal cations compared with benzocrown-ether-based analogues. We suggested that these problems can be resolved by using 1-aza-2,3-benzocrown ethers instead of *N*-phenylazacrown ethers.



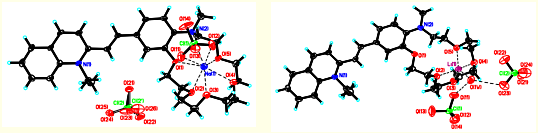
1 Synthesis of *N*-methylazacrown ether styryl dyes having an alkyl *N*-substituent in the heterocyclic moiety



2 X-Ray structures of *N*-methylazacrown ether styryl dyes



3 X-Ray Structures of complexes of *N*-methylazacrown ether styryl dyes



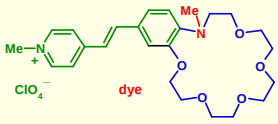
Complex with $NaClO_4$ | Complex with $LiClO_4$

4 Electronic spectroscopy study of dyes

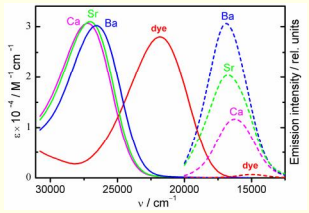
Stability constants of the complexes of dyes with metal cations

Dye	lg*K*						
	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
	3.12	2.72	-	5.30	5.24	4.71	4.24
	2.30	3.53	3.78	< 2	7.19	8.03	7.60
	2.50	3.87	4.11	< 2	7.67	8.34	8.08
	2.53	3.96	4.24	< 2	7.86	8.54	8.21
	2.58	4.01	4.29	< 2	7.94	8.72	8.29
	1.80	3.03	-	2.68	5.17	4.94	4.81

Spectrophotometric titration in MeCN.

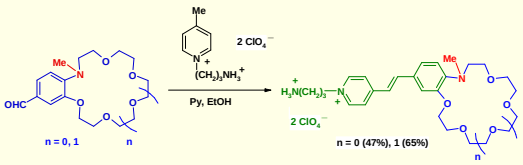


The fluorescence enhancement upon complexation with Ba^{2+}

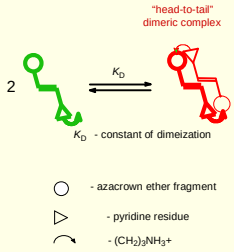


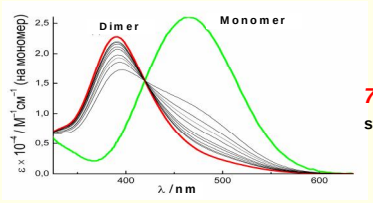
Absorption and emission spectra of dye and its complexes with Ca^{2+}, Sr^{2+}, and Ba^{2+} in MeCN.

5 Synthesis of *N*-methylazacrown ether styryl dyes having ammoniopropyl *N*-substituent in the heterocyclic moiety



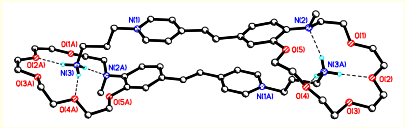
6 Spontaneous "head-to-tail" dimerization of the dyes



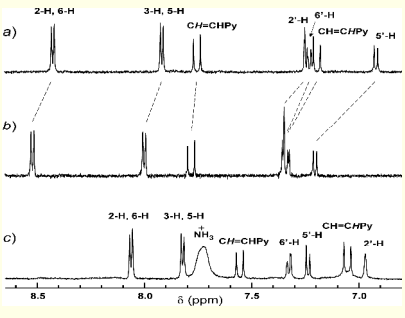


Absorption spectra of dye (n = 0) in MeCN/H_2O (47:3).

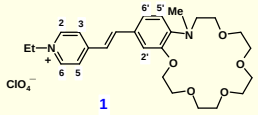
7 X-Ray structures of dimeric complex of aza-18-crown-6 ether styryl dye



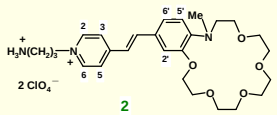
8 ^{1}H NMR spectroscopy studies



^{1}H NMR spectra of (*a*) dye **1**, (*b*) 1:5 mixture of dye **1** and $EtNH_3ClO_4$, and (*c*) dye **2** in MeCN-d_3.



1



2

log K_d = 8.2

Conclusions

1. New 2-benzothiazole-, 4-pyridine-, and 2- and 4-quinoline-based styryl dyes containing an *N*-methylbenzoaza-15(18)-crown-5(6)-ether moiety were synthesized.
2. The dyes having an alkyl *N*-substituent in the heterocyclic moiety are highly effective optical molecular sensors for alkali and alkaline-earth metal cations. They demonstrate strong cation-induced hypsochromic shifts in the absorption spectra (up to 136 nm) and cation-triggered emission with the enhancement factor reaching 61. The high degree of macrocycle pre-organization was found to be one of the factors determining the high cation-binding ability of the sensor molecules based on *N*-methylbenzoazacrown ethers.
3. Spontaneous "head-to-tail" dimerization of the dyes having ammoniopropyl *N*-substituent via the formation of numerous hydrogen bonds between the terminal NH_3^+ groups and crown-ether moieties was detected in MeCN solutions.

This work was supported by the Russian Foundation for Basic Research, the Russian Academy of Sciences, and the Royal Society of Chemistry.

1. Gromov S. P., Dmitrieva S. N., Vedernikov A. I., et al. *J. Org. Chem.*, 78, 9834 (2013).
2. Gromov S. P., Vedernikov A. I., Lobova N. A., et al. *J. Org. Chem.*, 79, 11416 (2014).