

Synthesis of cyanine dyes with terminal nitrogen-containing groups and their self-assembled supramolecular complexes with bis(18-crown-6)stilben

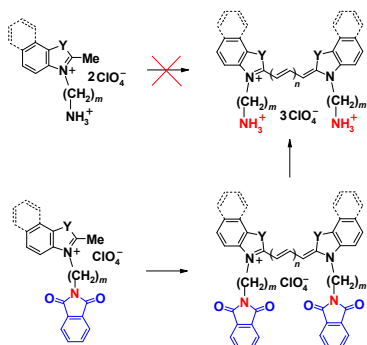
РОССИЙСКАЯ АКАДЕМИЯ НАУК
ЦЕНТР ФОТОХИМИИ

Fomina M.V., Nikiforov A.S., Vedernikov A.I., Kurchavov N.A., Gromov S.P.

Photochemistry Center of the RAS, Moscow, Russia

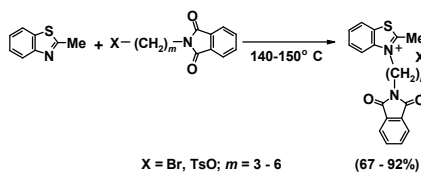
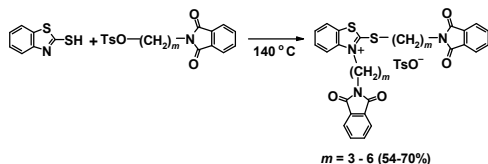
Introduction Cyanine dyes are well-known for their wide use in photographic materials; however, the interest in this class of compounds persists. The sensitivity of absorption and fluorescence of cyanine dyes to the medium determines good prospects for their use as probes, not only to study endogenous biomolecules but also to study the structure, kinetics, and thermodynamics of the formation of aggregates, supramolecular complexes and assemblies. In this connection, of interest are cyanine dyes with terminal ammonium groups in the *N*-substituents of heterocyclic residues. Methods for the preparation of cyanine dyes are based on the condensation of quaternary salts of heterocyclic bases containing an active methyl group in position 2 or 4 with C-electrophiles. The condensation is performed in the presence of bases. Cyanine dyes containing terminal ammonium groups in *N*-substituents cannot be prepared by direct condensation of quaternary heterocyclic salts containing ammonioalkyl groups due to side reactions. The use of phthalimide protecting group makes it possible to avoid undesirable processes.

1 Approach to the synthesis of symmetrical cyanine

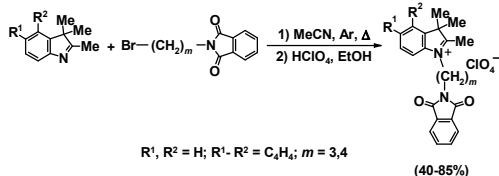


2 Synthesis the initial salts of heterocyclic bases

The benzothiazolium salts were prepared by fusing together of heterocyclic bases with phthalimidoalkyl derivatives.

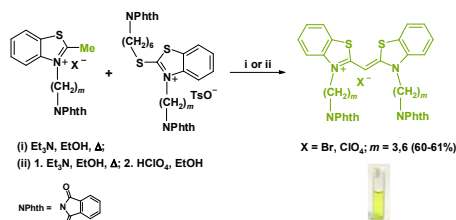


The indolium salts were prepared by the reaction of heterocyclic bases with phthalimidoalkyl derivatives; the reaction was carried out in acetonitrile under inert atmosphere.

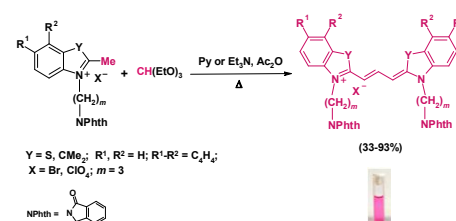


- S.P. Gromov, M.V. Fomina, A.S. Nikiforov, A.I. Vedernikov, L.G. Kuz'mina, J. A. K. Howard. *Tetrahedron*, 2013, 69, 5898.
- M.V. Fomina, A.S. Nikiforov, A.I. Vedernikov, A.N. Kurchavov, S.P. Gromov. *Mendeleev Commun.*, 2014, 24, 295.

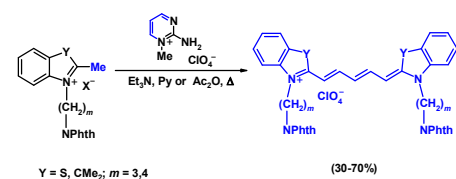
3 Synthesis of monomethine cyanine dyes



4 Synthesis of trimethine cyanine dyes

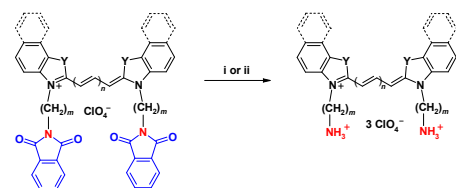


5 Synthesis of pentamethine cyanine dyes



6 Deprotection of the phthalimide group

Cyanine dyes with ammonioalkyl substituents at the heterocyclic nitrogen atoms were prepared after removal of the protecting groups by treatment hydrazine monohydrate or with methylamine.

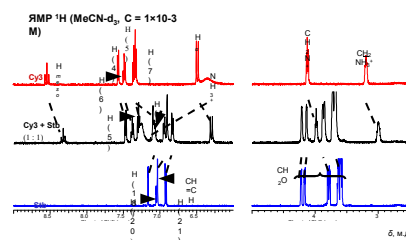


- MeNH₂, EtOH; 2. HClO₄, EtOH
- N₂H₄ · H₂O, CH₂Cl₂/MeOH; 2. HClO₄, EtOH

Yields of cyanine dyes with ammonioalkyl substituents

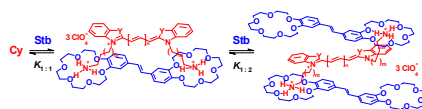
<i>n</i>	<i>m</i>	Y	R ¹ , R ²	Yield% (i)	Yield% (ii)
0	6	S	H, H	44	
1	3	S	H, H		17
1	3	CMe ₂	H, H	40	45
1	3	CMe ₂	H, H	25	
2	3	CMe ₂	C ₄ H ₄	42	
2	4	CMe ₂	H, H	51	37

6 Supramolecular complexes of cyanine dyes with bis(18-crown-6)stilben



7 1H NMR titration

The stoichiometry and the stability constants of the complexes obtained cyanine dyes with stilbene were determined using ¹H NMR titration in MeCN-d₃.



Stability constants of complexes of cyanine dyes with bis(18-crown-6)stilbene

Dye	<i>L</i> ^b	logK _{1:1}	logK _{1:2}
	17	8.1	1.7
	13	6.1	2.6
	15	6.4	2.1
	17	7.8	< 0.5

^b *L* = 5 + 2(*n* + *m*) is the number of atoms in the chain (shown in boldface) connecting two NH₃⁺ groups in the dye molecule.

Conclusions

- Synthesis of new symmetrical mono-, tri-, and pentamethine cyanine dyes with two *N*-ammonioalkyl substituents was developed.
- The obtained cyanine dyes with terminal ammonium groups on the *N*-substituents of heterocyclic residues can be employed as components for the design of light-sensitive supramolecular systems. We demonstrated the possibility to construct the supramolecular systems based on cyanine dyes with two ammonioalkyl *N*-substituents using their complexes with bis(18-crown-6)stilbene as an example. It was shown that the components form highly stable bimolecular and relatively unstable trimolecular complexes. The revealed trends of the formation of donor-acceptor complexes of cyanine dyes with bis(18-crown-6)stilbene can be used for the design of photoactive supramolecular systems.

We are grateful to Russian Scientific Foundation for financial support