Synthesis, structure and spectral properties of cyanine dyes containing terminal ammonium groups and photoactive supramolecular complexes based on them

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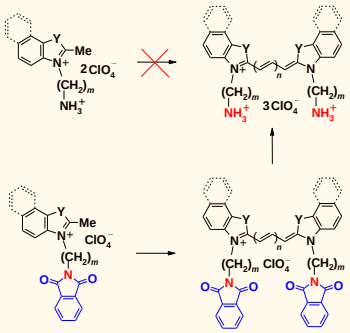
Introduction

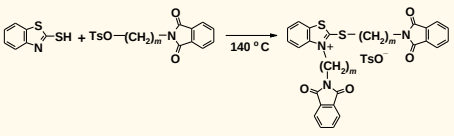
Self-assembled photoactive supramolecular systems formed by non-covalent interactions attract considerable attention. Cyanine dyes can be employed as light-sensitive components for the design of such supramolecular systems. In order to elucidate the possibility to construct photoactive "host-guest" complexes based on cyanine dyes as a guest and the influence of their structure on the properties of supramolecular complexes, we synthesized cyanine dyes with ammonioalkyl substituents at the heterocyclic nitrogen atoms with yield up to 51%. Structure obtained dyes was determined by NMR-, IR-, UV spectroscopy, X-ray diffraction data, and elemental analysis. The presence of primary ammonium groups capable of hydrogen bonding enables self-assembly of dyes with macroheterocyclic molecules containing electron-donating oxygen heteroatoms to form supramolecular complexes. Complexation was studied using absorbtion, luminescence and ^{1}H NMR spectroscopy.

1 Approach to the synthesis of symmetrical cyanine dyes

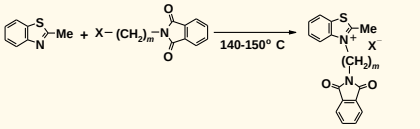


2 Synthesis the initial salts of heterocyclic bases

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

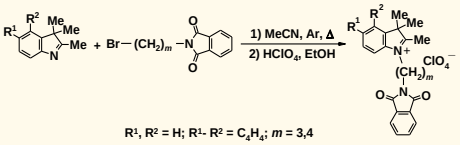


m = 3 - 6 (54-70%)



X = Br, TsO; *m* = 3 - 6 (67 - 92%)

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



R^1, R^2 = H; R^1- R^2 = C_4H_4; *m* = 3,4 (40-85%)

1. Громов С. П., Фомина М. В., Никифоров А. С. "Симметричные цианиновые красители с терминальными азотсодержащими группами в N-заместителях гетероциклических остатков в качестве люминофоров и способ их получения" // Патент РФ. № 2472822.
2. S.P. Gromov, M.V. Fomina, A.S. Nikiforov, A.I. Vedernikov, L.G. Kuz'mina, J. A. K. Howard. *Tetrahedron*, 2013, 69, 5898.
3. M.V. Fomina, A.S. Nikiforov, A.I. Vedernikov, N.A. Kurchavov, S.P. Gromov. Self-assembly of supramolecular complexes of cyanine dyes containing terminal ammonium groups with bis(18-crown-6)stilbene. Mendeleev. Commun. 2014, 24, 295-297.

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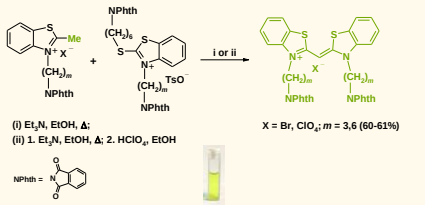
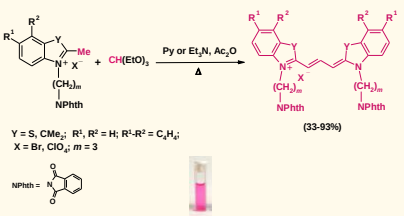
3 Synthesis of monomethine cyanine dyes



(i) Et_3N, EtOH, Δ;
(ii) 1. Et_3N, EtOH, Δ; 2. $HClO_4$, EtOH

X = Br, ClO_4; *m* = 3,6 (60-61%)

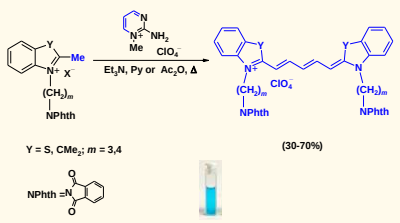
4 Synthesis of trimethine cyanine dyes



Y = S, CMe_2; R^1, R^2 = H; R^1-R^2 = C_4H_4;
X = Br, ClO_4; *m* = 3

(33-93%)

5 Synthesis of pentamethine cyanine dyes

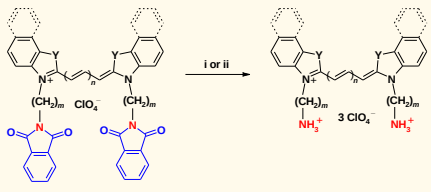


Y = S, CMe_2; *m* = 3,4

(30-70%)

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.

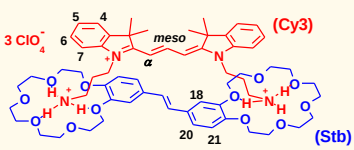


(i) 1. $MeNH_2$, EtOH; 2. $HClO_4$, EtOH
(ii) 1. N_2H_4 H_2O, CH_2Cl_2/MeOH; 2. $HClO_4$, EtOH

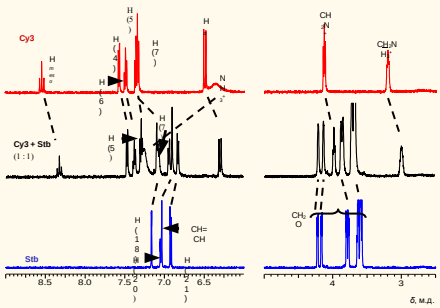
Yields of cyanine dyes with ammonioalkyl substituents

n	*m*	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_4H_4	42	
2	4	CMe_2	H,H	51	37

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

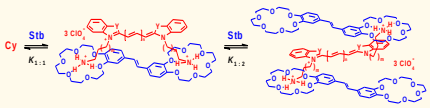


ЯМР ^{1}H (MeCN-d_3, C = 1 10^{-3} M)

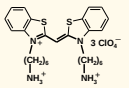
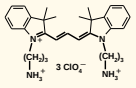
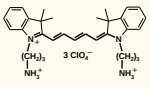
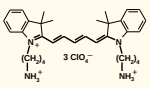


7 ^{1}H NMR titranion

The stoichiometry and the stability constants of the complexes the obtained cyanine dyes with stilbene were determined using ^{1}H NMR titration in MeCN-d_3.



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

Dye	*L* [b]	log$K_{1:1}$	log$K_{1:2}$
	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 NH_3^+ groups in the dye molecule.

Conclusions

1. Synthesis of new symmetrical mono-, tri-, and pentamethine cyanine dyes with two N-ammonioalkyl substituents was developed.
2. 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.
3. The formation of supramolecular complexes of different stoichiometry was discovered.
4. Their stability constants were determined.

The synthesized cyanine dyes and supramolecular systems based on them may be used as components of photoactive supramolecular devices, optical molecular sensors.

LABORATORY OF SYNTHESIS AND SUPRAMOLECULAR CHEMISTRY OF PHOTOACTIVE COMPOUNDS

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