

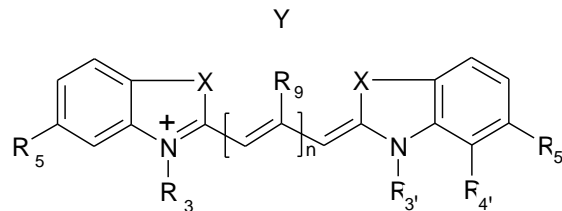


The Triplet States of the Dimers of Polymethine Dyes

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The Objects and Methods

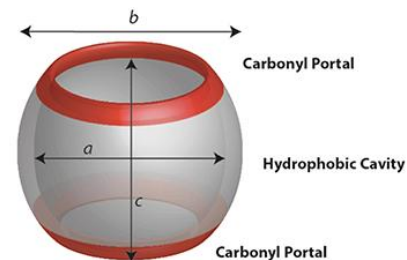
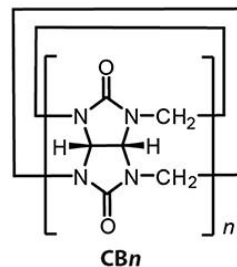
Polymethine dyes



Dye	R _{3,3'}	R _{4'}	R _{5'}	R ₅	R ₉	X	Y	n
Dye1	C ₂ H ₅	H	H	H	CH ₃	S	I ⁻	1
Dye2	C ₂ H ₅	H	H	H	H	S	I ⁻	1
Dye3	C ₂ H ₅	H	Cl	Cl	C ₂ H ₅	S	Cl ⁻	1
Dye4	(CH ₂) ₃ SO ₃ ⁻	H	OCH ₃	OCH ₃	C ₂ H ₅	S	C ₅ H ₅ NH ⁺	1
Dye5	CH ₃	H	H	H	H	C(CH ₃) ₂	I ⁻	2

Cucurbit[8]uril (CB8)

Cucurbiturils are efficient host molecules in molecular recognition and have a particularly high affinity for positively charged or cationic compounds. High association constants with positively charged molecules are attributed to the carbonyl groups that line each end of the cavity and can interact with cations.



n	a, Å	b, Å	c, Å	Cavity volume, Å ³
8	8,8	6,9	9,1	479

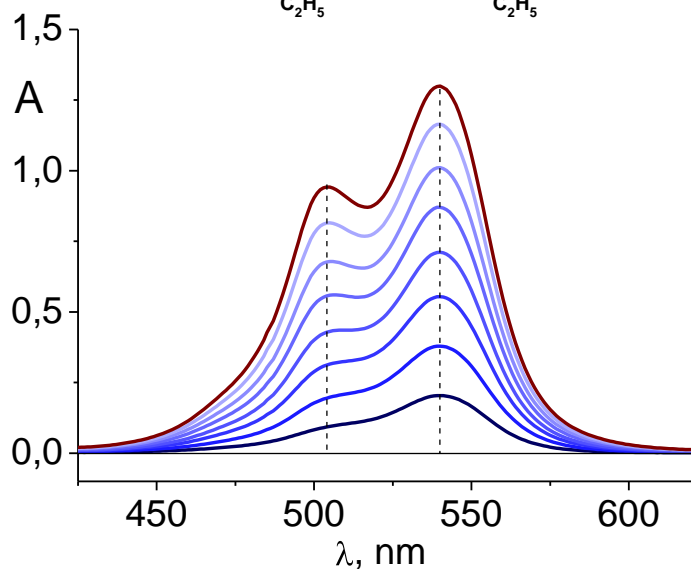
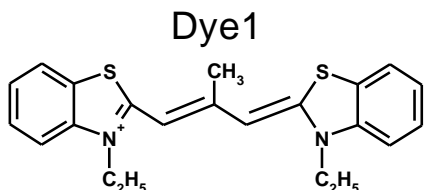
Methods

- Spectroscopy

- Nanosecond laser photolysis

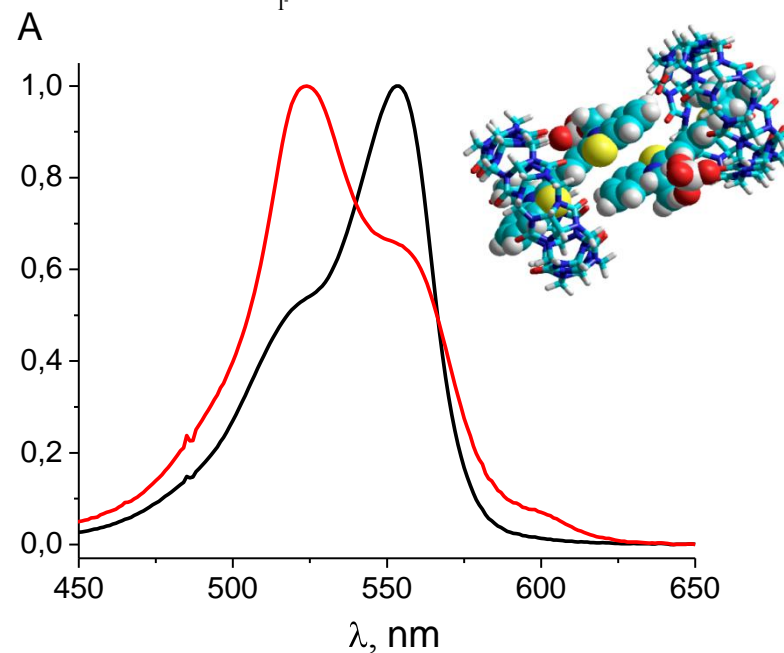
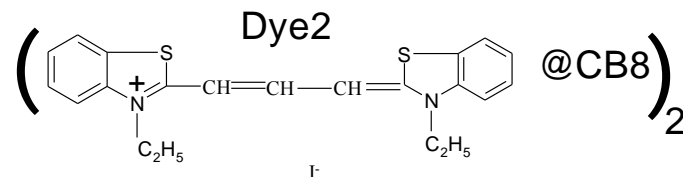
Dimers formation

Dimers in water



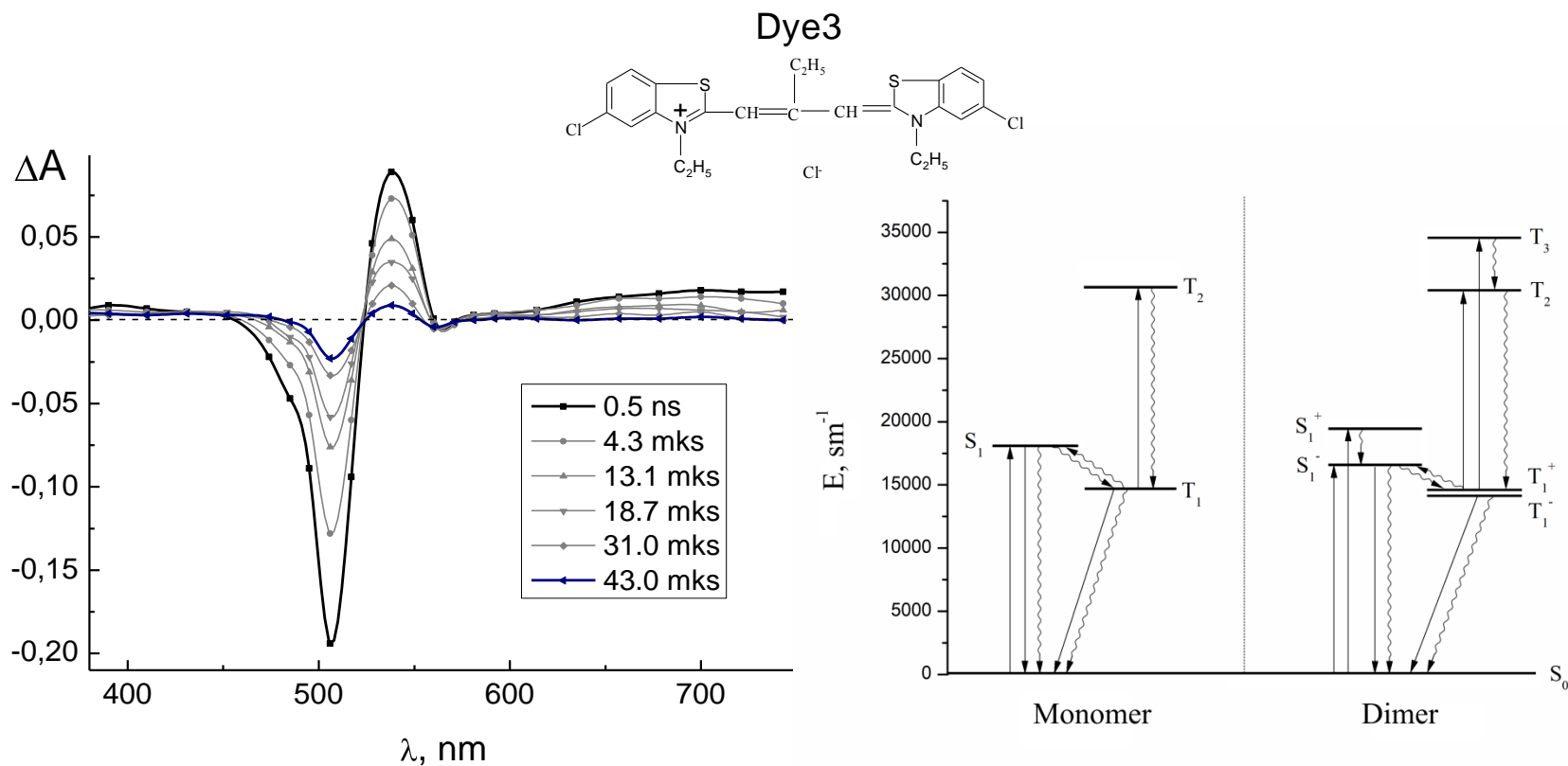
Absorption spectra of Dye1 in water. Concentration of the dye: (5.5×10^{-6} 3.5×10^{-5}) mol/L. The dimerization constant calculated from the Harris-Hobbs equation was $1.1 \cdot 10^4$ L/mol.

Complexation with cucurbit[8]uril



Normalized absorption spectra of monomers in water (**black**) and dimeric complexes of Dye2 with CB8 of the composition 2:2 (**red**). The inset shows the optimized structure of dimeric complexes (Dye2@CB8)₂.

Triplet-Triplet Absorption

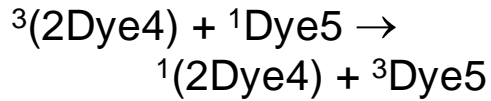


Time-resolved difference T-T absorption spectra of the dimer of Dye3. The inset shows the time of the measurement.

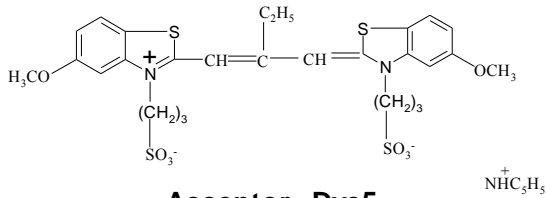
Diagram of the excited singlet and triplet states of monomers and dimers of Dye3. Solid lines – radiative transitions, wavy lines – radiationless decay.

Photoprocesses in polymethine dyes

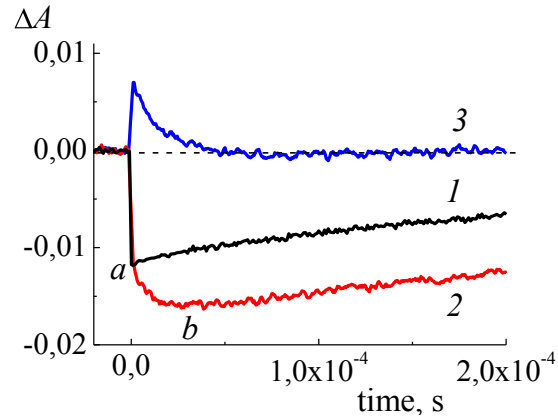
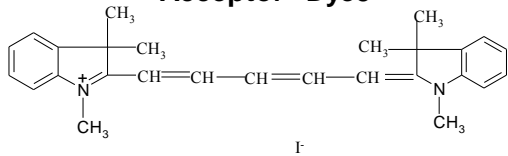
Triplet-triplet energy transfer



Donor - dimer of Dye4



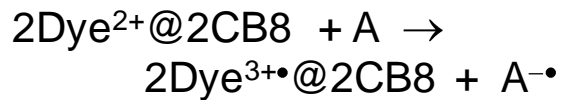
Acceptor - Dye5



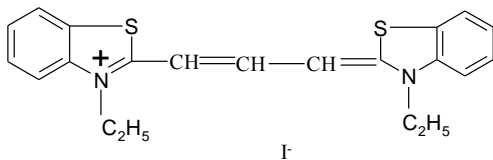
- 1 - photoisomerization of Dye5
- 2 - formation of T-state of Dye5 (a-b)
- 3 - decay of T-state of 2Dye4 in the presence of Dye5

The rate constant of triplet-triplet energy transfer is $5 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$.

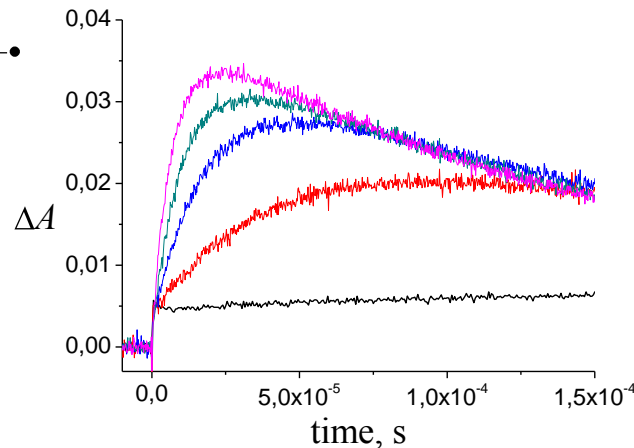
Photoinduced electron transfer



Dye2



Acceptor (A) -
1,4-dinitrobenzene



The formation of $2\text{Dye}^{3+\bullet}@2\text{CB8}$ in the absence and in presence of 1,4-dinitrobenzene (5×10^{-6} to $2 \times 10^{-5} \text{ mol/L}$).

The rate constant of photoinduced electron transfer is $3 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$.

Financing

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Based on the materials of the report an article is being prepared in the journal Russian Chemical Bulletin.