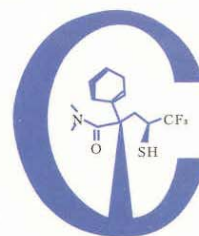


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Третья молодежная  
школа-конференция  
по органическому синтезу  
*Third Youth School-Conference  
on Organic Synthesis  
(YSCOS-3)*



**"ОРГАНИЧЕСКИЙ СИНТЕЗ В НОВОМ  
СТОЛЕТИИ"**  
*"Organic Synthesis in the New Century"*



**МАТЕРИАЛЫ КОНФЕРЕНЦИИ**  
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**ABSTRACTS OF PAPERS**  
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ТРЕТЬЕЙ МОЛОДЕЖНОЙ ШКОЛЫ-КОНФЕРЕНЦИИ ПО ОРГАНИЧЕСКОМУ  
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## STATIC AND DYNAMIC FLUORESCENCE OF DIPHENYLHEXATRIENE-CYCLODEXTRINE "GUEST-HOST" NANOSTRUCTURE

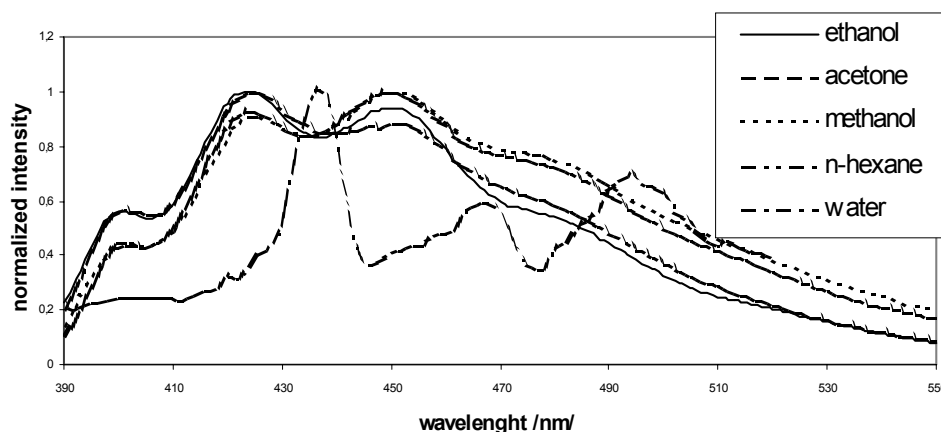
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A development of laser technology pushed the limits of time-resolved techniques dealing with dynamics of chemical processes. An observation of a chemical reaction in real time [1] started a wide spreading use of time-resolved experiments in all branches of chemistry. Those experiments span from a solvation dynamics [2], through excited electron relaxation on solid metallic surfaces [3], to isomerization dynamics in nanocavities [4]. Our experiment focuses on static and dynamic fluorescence as a function of interaction between solute and solvent. The main relaxation channel of this process is the interaction between charge distribution of solute and dipoles of solvent molecules. The result of this interaction is reorientation of solvent, a consequence of dielectric reaction as a measure of dipoles reorientation polarization response. The involved processes are internal relaxation, interaction with the environment and the fluorescence itself. The fastest process is the internal conversion and just this aspect of fluorescence dynamics is possible to measure with an experimental set-up providing picosecond time resolution.

An investigated subject of our solvation experiments is supramolecular host-guest inclusion complex [5,6]. The model host-guest complex is based on diphenylhexatriene-cyclodextrin. Complexation of mostly hydrophobic guest molecules with host molecules is a widely found phenomenon in chemistry. Cyclodextrins [7], as well known host molecules, are cyclic oligosaccharides consisting of six ( $\alpha$ -), seven ( $\beta$ -) or eight ( $\gamma$ -)  $\alpha$ -1,4-glycosidically linked glucopyranose subunits. They form truncated cone shaped structure providing a hydrophobic inner cavity and a hydrophilic outer cavity. The cyclodextrin (CD) host serves as hydrophilic envelope for the guest and increases thus the solubility of the guest in water and provides additional mechanical, optical, and chemical protection. As a guest molecule was selected 1,6-diphenylhexatriene (DPH). This molecule not only provides on own fluorescence signal and also that linked with CD-s to form a nanowire [8].



**Figure 1.** Fluorescence intensity of the DPH in different solvents

The host-guest system was initially characterized by using steady-state fluorescence spectroscopy (Fluorolog 3.11.). The excitation and fluorescence spectra of DPH were measured in ethanol, methanol, acetone, *n*-hexane and water. The fluorescence spectra are shown in Fig. 1. The wavelength maxima of the DPH structure are 400, 423 and 451 nm, 402, 424 and 450 nm, 404, 426 and 452 nm, and 402, 425 and 450 nm in ethanol, methanol, acetone, and *n*-hexane, respectively. The intensity of fluorescence changes with the concentration as follows. The solutions of ethanol, methanol, acetone, and *n*-hexane were measured in the concentration range from  $5 \times 10^{-4}$  to  $10^{-6}$  M and their intensities decreased from 716000 to 57000 photons  $s^{-1}$ , 341000 to 70500 photons  $s^{-1}$ , 380000 to 28500 photons  $s^{-1}$ , and 166000 to 17000 photons  $s^{-1}$ , respectively. The measurement of DPH fluorescence was also performed in water. The aqueous DPH solution of approximately  $10^{-8}$  M concentration resulted in different shape with clear peaks at 438, 468 and 494 nm and shoulders with maxima comparable with other solvents. Such a different shape can be explained by the extremely low solubility of DPH in water. Most probably, the shoulders represent a presence of DPH solvated in water and the peaks are result of the DPH aggregates formed due to low solubility.

The formation of the host-guest complexes with  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD-s and DPH was investigated. The formation of DPH-CD nanostructure was previously observed by using anisotropy measurements [8]. The DPH-CD complex and its fluorescence relaxation dynamics were investigated by using femtosecond time-resolved fluorescence. The applied technique is based on up-conversion of the fluorescence signal with the delayed probing signal. The fundamental pulse used both for the fluorescence excitation (doubled before) and the probing, are generated from the Ti-sapphire oscillator. The time resolution of this technique is approximately 100 fs. The exponential fitting parameters of the measured fluorescence relaxation of DPH in acetone are shown in Table 1, the first part belongs to the long-time range (600 ps) dynamics and the second part belongs to the short-time range (90 ps) dynamics.

**Table 1.** Relaxation times of fluorescence of DPH in acetone

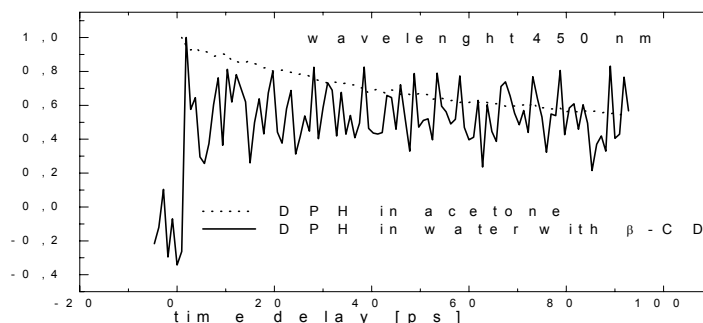
Long-time relaxation (600 ps)				Short-time relaxation (90 ps)	
$\lambda$ , nm	$\tau_1$ , ps	$\tau_2$ , ps	$a_1/a_2$	$\lambda$ , nm	$\tau_1$ , ps
425	18±12	69±51	2,1906	425	28,8±3,2
450	62±58	551±1032	0,4892	450	44,2±3,0
475	32±22	124±72	0,5668	475	45,2±2,0

$\tau_1, \tau_2$  – exponential relaxation times

$a_1, a_2$  – fluorescence constants

$\lambda$  - fluorescence wavelength

The time-resolved fluorescence dynamics of the DPH-CD complex was also investigated. The solubility of the water-CD mixture was enhanced by acetone as co-solvent. In this way, it was possible to obtain enough fluorescence signal for time-resolved measurement. However this data quality was lower as in the case of acetone solution. An example of the differences in fluorescence relaxation dynamics between DPH in acetone and DPH in water with  $\beta$ -CD are shown in Fig. 2.



**Figure 2.** Relaxation of DPH in acetone and in water with  $\beta$ -CD

The measured time-resolved data showed weaker relaxation process in the case of water-CD, which would originate from the higher conformational stability of DPH-CD host-guest complexes.

#### References

- [1] A. H. Zewail, *Femtochemistry Ultrafast Dynamics of the Chemical Bond*. Vol. I, World Scientific Publishing Co., Inc., New Jersey, 1994.
- [2] M. L. Horng, J.A. Gardecki, A. Papazyan, M. Maroncelli, *J. Phys. Chem.*, 99, (1995) 17311.
- [3] D. Velic, A. Hotzel, M. Wolf, G. Ertl, *J. Chem. Phys.*, 109, (1998) 9155.
- [4] A. Douhal, T. Fiebig, M. Chachisvilis, A. H. Zewail, *J. Phys. Chem.*, 102, (1998) 1657.
- [5] D. Velic, M. Knapp, G. Koehler, *J. Mol. Struct.*, 598, (2001) 45.
- [7] K. A. Connors, *Chem. Rev.*, 97, (1997) 1325.
- [6] G. Grabner, K. Rechthaler, B. Mayer, G. Koehler, K. Rotkiewicz, *J. Chem. Phys. A*, 104, (2000) 1365.
- [8] G. Li, L. B. McGown, *Science*, 264, (1994) 249.