Speaker – Prof. Khodonov A.A.

Synthesis and photochromic behavior study of the new podand

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Design and development of methods for obtaining new hybrid photochromic ligands (HPL) with ionophore fragments, and a comprehensive study of their photochromic behavior and spectral-kinetic characteristics in the presence of various cations

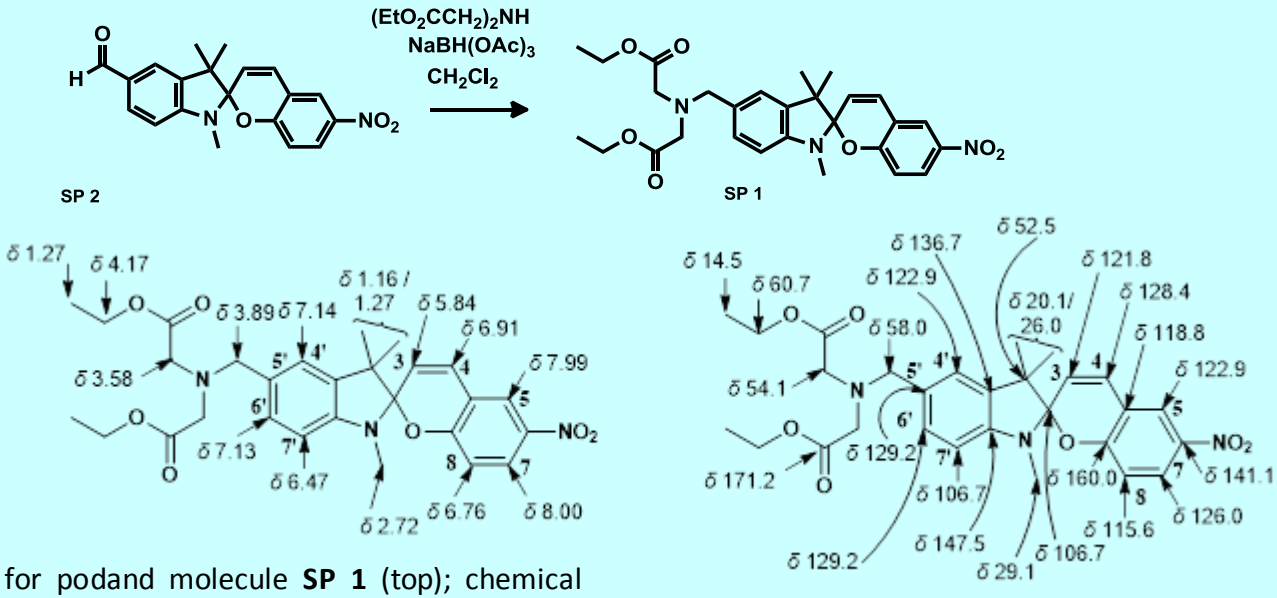

Fig. 1. Synthetic scheme for podand molecule **SP 1** (top); chemical shifts of signals in ^{1}H-NMR and ^{13}C-NMR spectra of photochromic podand **SP 1** in $CDCl_3$ (bottom).

Photochromic ionophores and light-driven artificial receptors, which allow controlling cation- or ligand-binding process as well as the properties of generated products by the illumination of the sample with light of distinct wavelength, attract particular attention for the application in various areas.

We selected the spirobenzopyran derivative **SP1** as a scaffold for target ionophoric podand synthesis. Several examples of such photochromic systems which contain various types of reactive anchor groups with affinity to the cations are known. Among them the diverse derivatives of crown-ethers, podands, chelates, iminodiacetates, N-heterocycles, thiols, bipyridines and dendrimers were described. To provide the capability of selective binding with cations or other types of charged ligands we introduce a “molecular address” – a fragment of iminodiacetate diethyl ester with ability to bind to metal cations, at the C5′-position of the podand molecule.

In this study we used a one pot synthetic procedure for reductive amination of 5'-formyl-6-nitrospiropyran (SP2) by the sodium triacetoxyborohydride in the presence of the aminocomponent excess. The target spirobenzopyran (SP1) was synthesized in the preparative amounts (43% yield); their structure was characterized by a number of physical-chemical analysis methods.

The study of the photochromic properties of the podand (SP1) showed that the principal behaviour of this compound did not differ from that of other 6-nitro-substituted spirobenzopyrans.

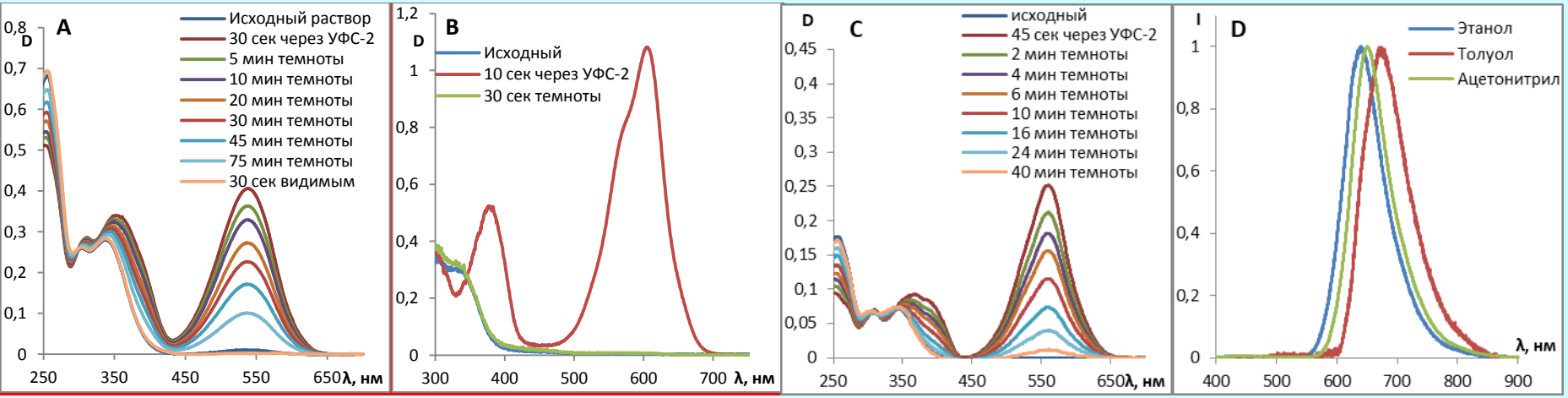

Fig. 1. Absorption spectra of photochromic podand (SP 1) in a solution of ethanol (A) and toluene (B), acetonitrile (C), 25 C.
(D) fluorescence spectra of the merocyanine form of the photochromic ligand (SP 1) in solution of ethanol, toluene and acetonitrile, obtained using a USB4000-FL spectrofluorometer module, 25^{0}C. The conditions for excitation of a xenon lamp light through UFS-2 (280-370 nm) filter.

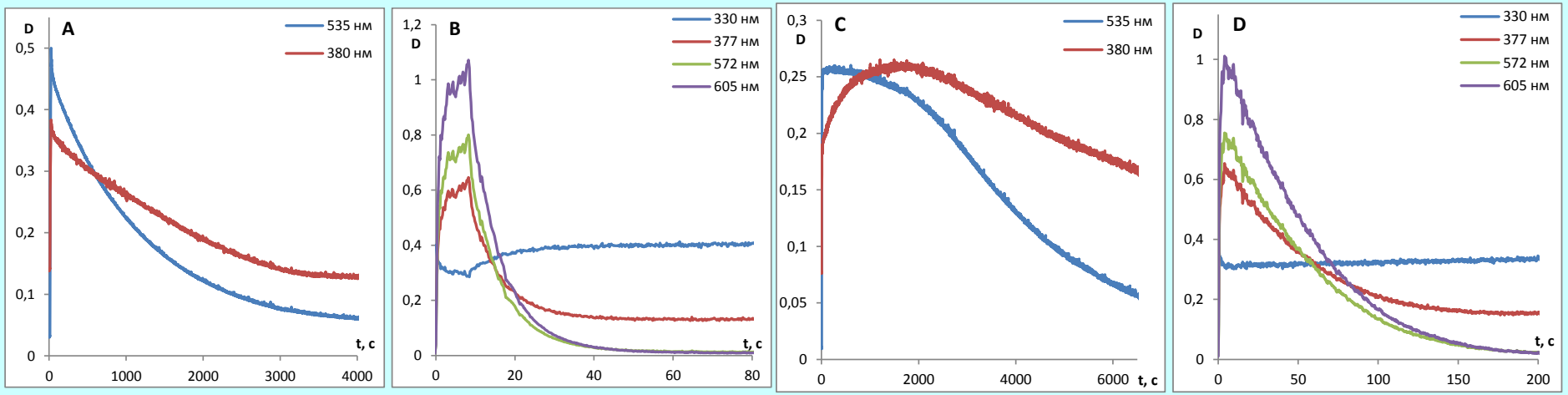

Fig. 2. Kinetics of dark bleaching of the photochromic podand **SP1** in ethanol (A) and in toluene (B): (A) 1 – at 380 nm, 2 – at 535 nm ; (B) 1 – at 330 nm, 2 – at 377 nm, 3 – at 572 nm, 4 – at 605 nm.
The kinetics of photodegradation of the photochromic podand **SP1** in ethanol (C) and in toluene (D): (C) 1 – at 380 nm, 2 – at 535 nm; (D) 1 – at 330 nm, 2 – at 377 nm, 3 – at 572 nm, 4 – at 605 nm.

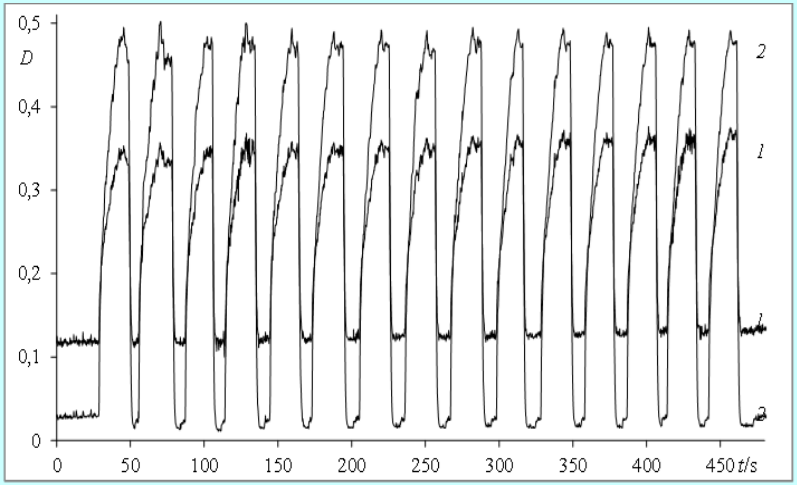

Fig. 3. Reproductibility of the kinetics of photocolouring/photobleaching of the photochromic dopand **SP1** in ethanol at 25^0C: 1 – at 380 nm, 2 – at 535 nm.

Table 1. Spectral and kinetic characteristics of photochromic podand (**SP 1**) in ethanol and in toluene

Solvent	λ_A, nm	λ_B, nm	ΔD_B^{phot}	λ_{fl}, nm	k_{BA}^{db}, s^{-1}	$t_{1/2}$, s
Ethanol	337, 304, 255	538, 351, 310, ~254	0.66	636	$8.73*10^{-4}$	4000
Toluene	334	605, ~570sh, ~337	3.53	666	$1.23*10^{-1}$	28
Acetonitrile	336	561	1.47	650	$1,29*10^{-3}$	3000

The photochromic behavior of the synthesized compound in solutions of ethanol or acetonitrile in the presence of cations of varying nature was investigated.

The spectral-kinetic study of photochromic behavior and fluorescence in organic solvents with different polarity has been carried out both in presence and in absence of metal cations.

We used nitrates of bivalent and trivalent cations (Ca, Co, Ni, Cu, Al, Cr, La, Fe, Eu, Ce) in a podand ratio (**SP 1** – Me^{n+} 1:10). There is a pronounced selectivity of the ionophore fragment of the podand molecule (SP 1) for the formation of complexes with salts of trivalent cations. The complexes have different stability in the dark, but are instantly destroyed when illuminated with visible light. Since the closed spiro form of podand (SP 1) is incapable of spontaneous formation of complexes with metal salts in the dark, it was necessary to generate the merocyanine form by illuminating the sample with the light of a xenon lamp through an UFS-2 light filter (280-370 nm). When cations were added to the solution of the photoinduced MC form of spiropyran, in some cases, for La, Al, Cr salts, a strong hypsochromic shift of the absorption band maximum was observed (the difference between the absorption band maxima of the photoinduced forms of the compound (SP 1) and its complexes with cations, $\Delta\lambda_B$, approximately 120 nm) (see Fig.). Thus, it was shown for the first time that podand (SP 1) with an ionophore iminodiacetate fragment possesses photocontrolled sensory properties.

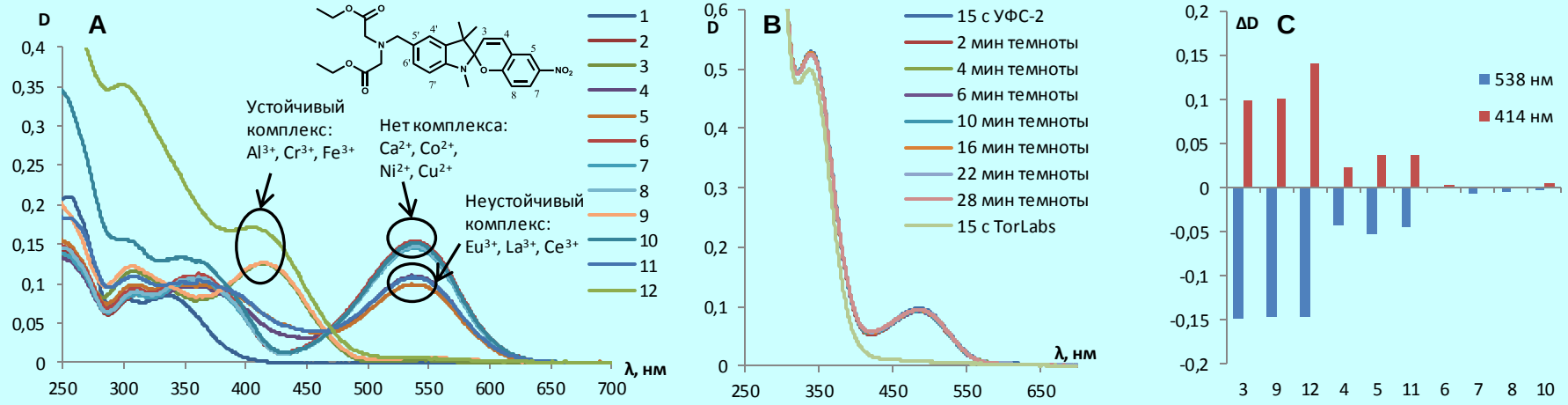

Fig. 4. A -Absorption spectra of podand (SP 1) in the presence of metal salts in ethanol.

Lines: 1 - spiro form (SP 1), 2 - photoinduced merocyanine form (SP 1), 3–12 - photoinduced merocyanine form (SP 1) in the presence of excess metal salt (cation: SP concentration ratio 1 – 10)

Used metal salts: 3 - $Al(NO_3)_3$, 4 - $La(NO_3)_3$, 5 - $Eu(NO_3)_3$, 6 - $Ca(NO_3)_2$, 7 - $Co(NO_3)_2$, 8 - $Ni(NO_3)_2$, 9 - $Cr(NO_3)_3$, 10 - $Cu(OAc)_2$, 11 - $Ce(NO_3)_3$, 12 - $Fe(NO_3)_3$.

B- Kinetics of the decomposition of the complex of podand (SP 1) with $La(NO_3)_3$ in acetonitrile in the range from 0 to 30 min. Illumination of the sample with visible light from a ThorLabs 20 W halogen lamp for 15 s leads to the complete collapse of the complex.

(**C**) Changes in the optical density at 538 and 414 nm of solutions of podand (SP 1) in ethanol in the presence of salts of various metals.

Research results

1. The new synthetic method for the preparation of new spiropyran with ionogenic fragment in 5'-position has been developed.

2. The spectral-kinetic study of photochromic behavior and fluorescence properties study in organic solvents with different polarity has been carried out without and in the presence of metal cations.

3. It was shown for the first time that a podand SP1 with an ionophore iminodiacetate fragment has selective sensory properties.

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