ELECTRO- AND PHOTOELECTRIC PROPERTIES OF NEW PHOTOSENSITIVE THIN FILM STRUCTURES BASED ON ANIONIC σ-COMPLEXES

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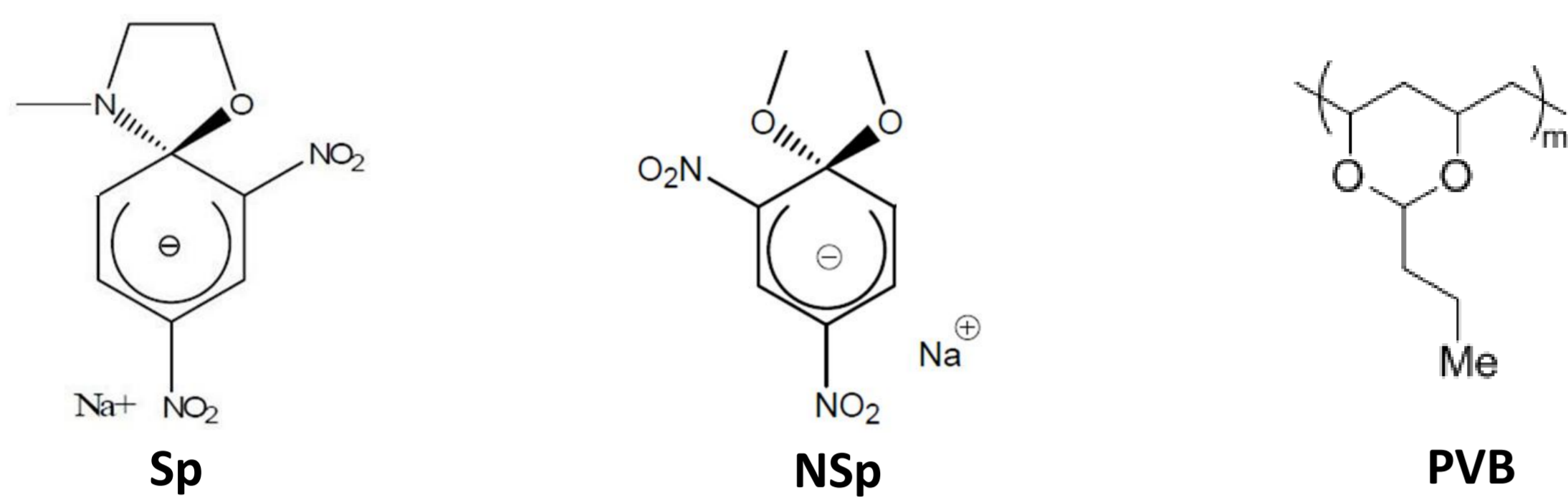
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The colored spirocyclic (**Sp**) and non-spirocyclic (**NSp**) anionic sigma complexes – dinitro substituted aromatic alkoxyl Meisenheimer complexes – were synthesized. The novel photosensitive thin film structures based on these anionic sigma complexes and their composites with dielectric polymer (polyvinyl butyral) matrices have been prepared. Their spectral, electric and photoelectrophysical properties have been investigated.

It was established that all obtained thin film structures are characterized by a high level of ionic conductivity. It was shown, that all studied film structures exhibit photovoltaic effect and n-type photoconductivity under illumination by light from the long-wavelength edge of the synthesized anionic σ-complexes absorption region. The features of electrophysical, photophysical and photoelectric properties of the obtained thin film structures, as well as the possible nature of the photovoltaic effect and charge carriers photogeneration mechanisms are discussed.

The investigated colored anionic σ-complexes can be used as photosensitive components of novel photoconductive composite materials for molecular photonics applications.

OBJECTS OF INVESTIGATION

Sp   **NSp**   **PVB**
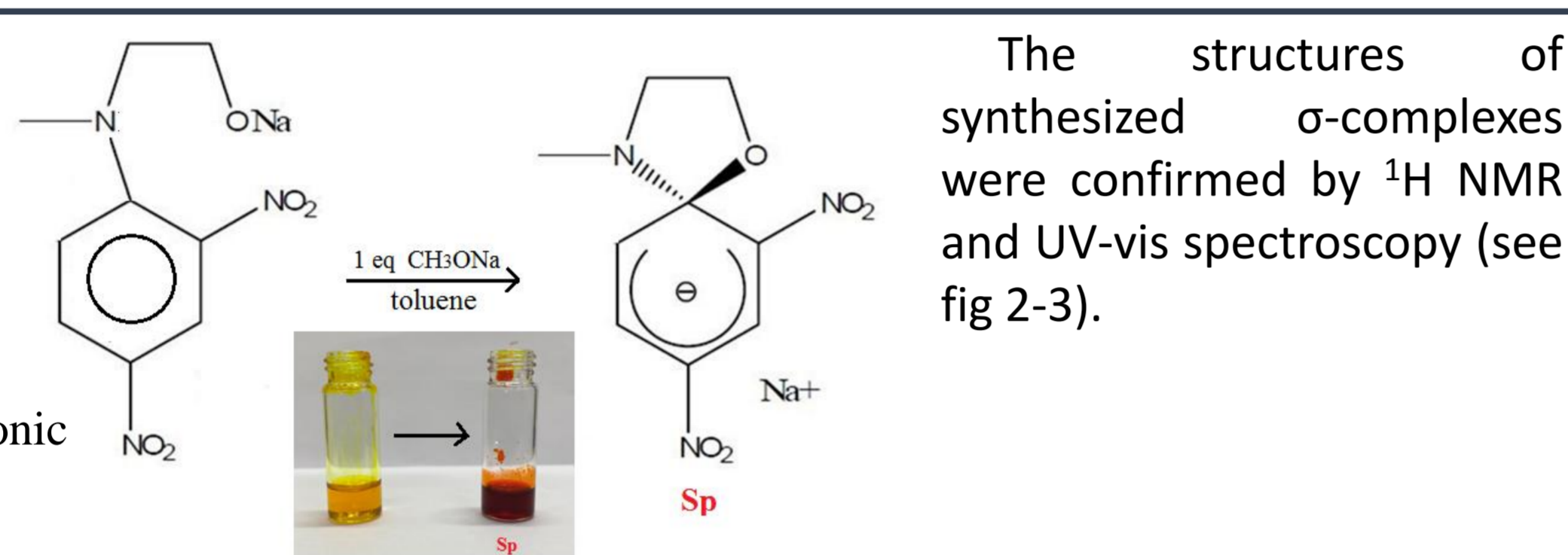
RESULTS AND DISCUSSION

The structures of synthesized σ-complexes were confirmed by ^{1}H NMR and UV-vis spectroscopy (see fig 2-3).

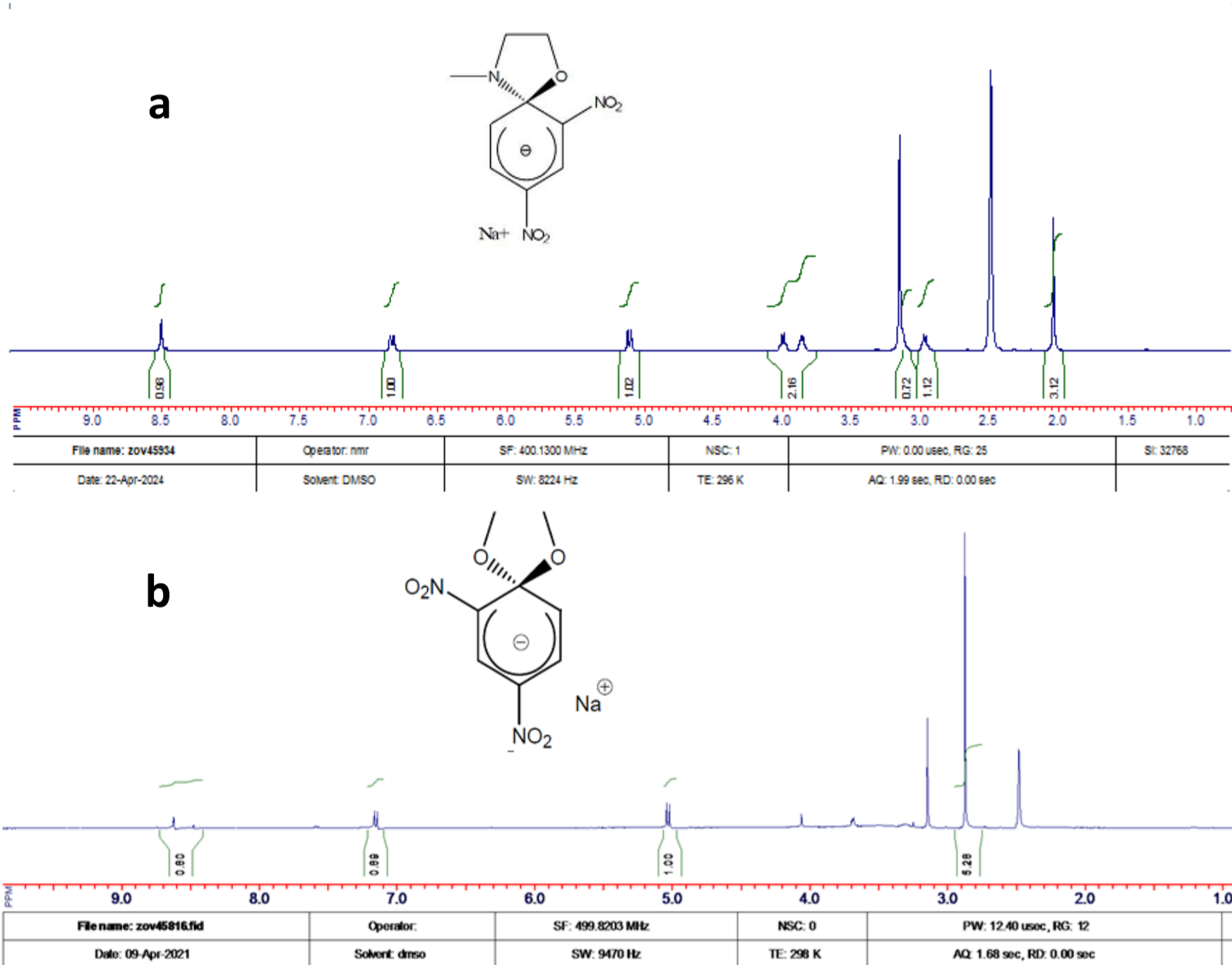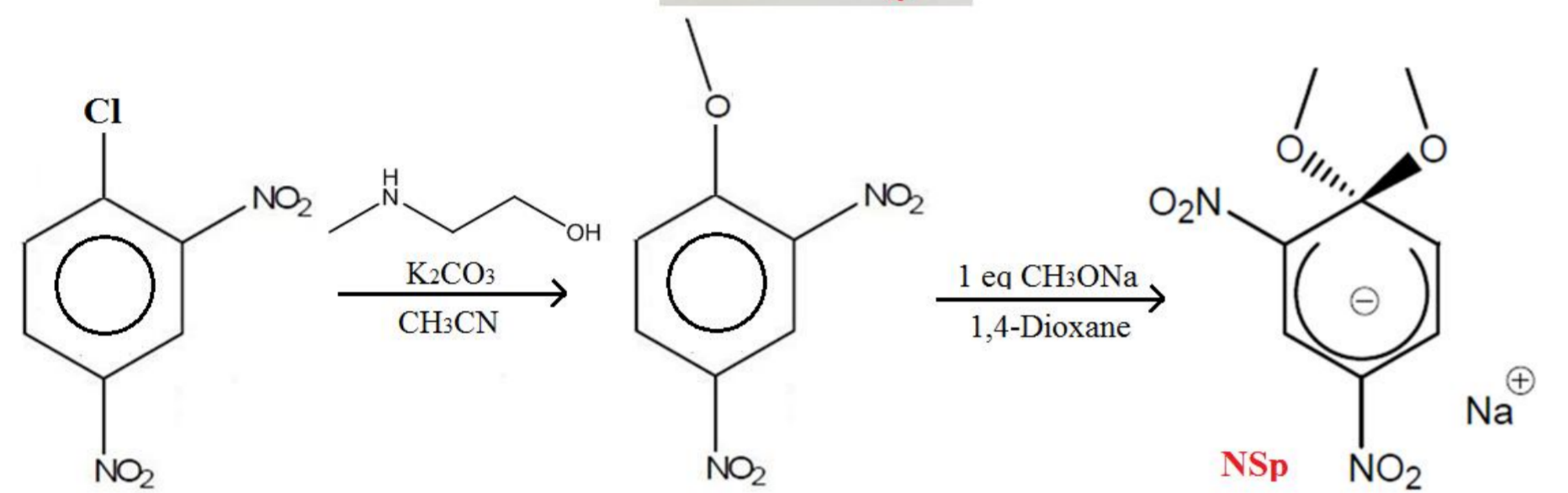Fig. 1. Scheme of synthesis of anionic σ-complexes **Sp** and **NSp**.

Fig. 2. ^{1}H NMR spectra of Sp (**a**) and NSp (**b**) in DMSO-d_6.

Novel photosensitive thin film (L ~ 1,5 micron) polymeric compositions based on polyvinyl butyral (PVB) doped with 50wt. % of obtained anionic σ-complexes were prepared. Their spectral, electric and photoelectrophysical properties have been investigated.

The samples were prepared as structures with a free surface [glass substrate – PCF], [glass substrate – transparent electroconducting ITO layer – PCF], and as the sandwich structures [glass–ITO–PCF–ITO-glass]. Concentrations of complexes in all films was 50 wt. %.
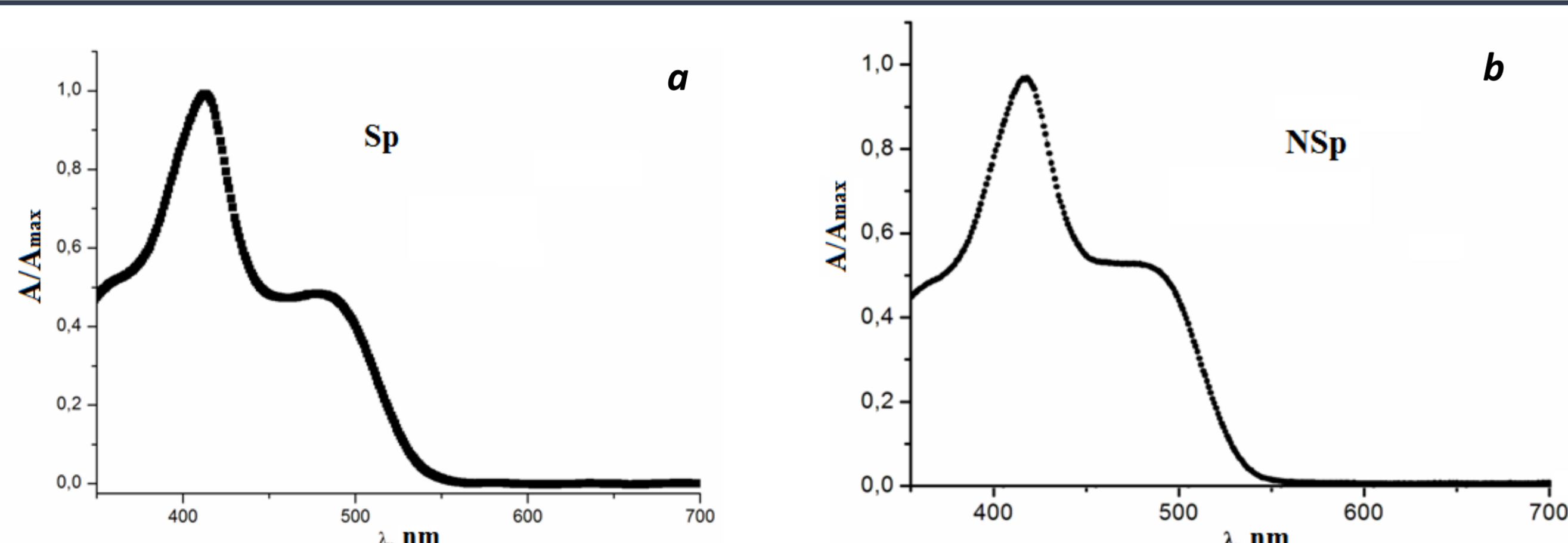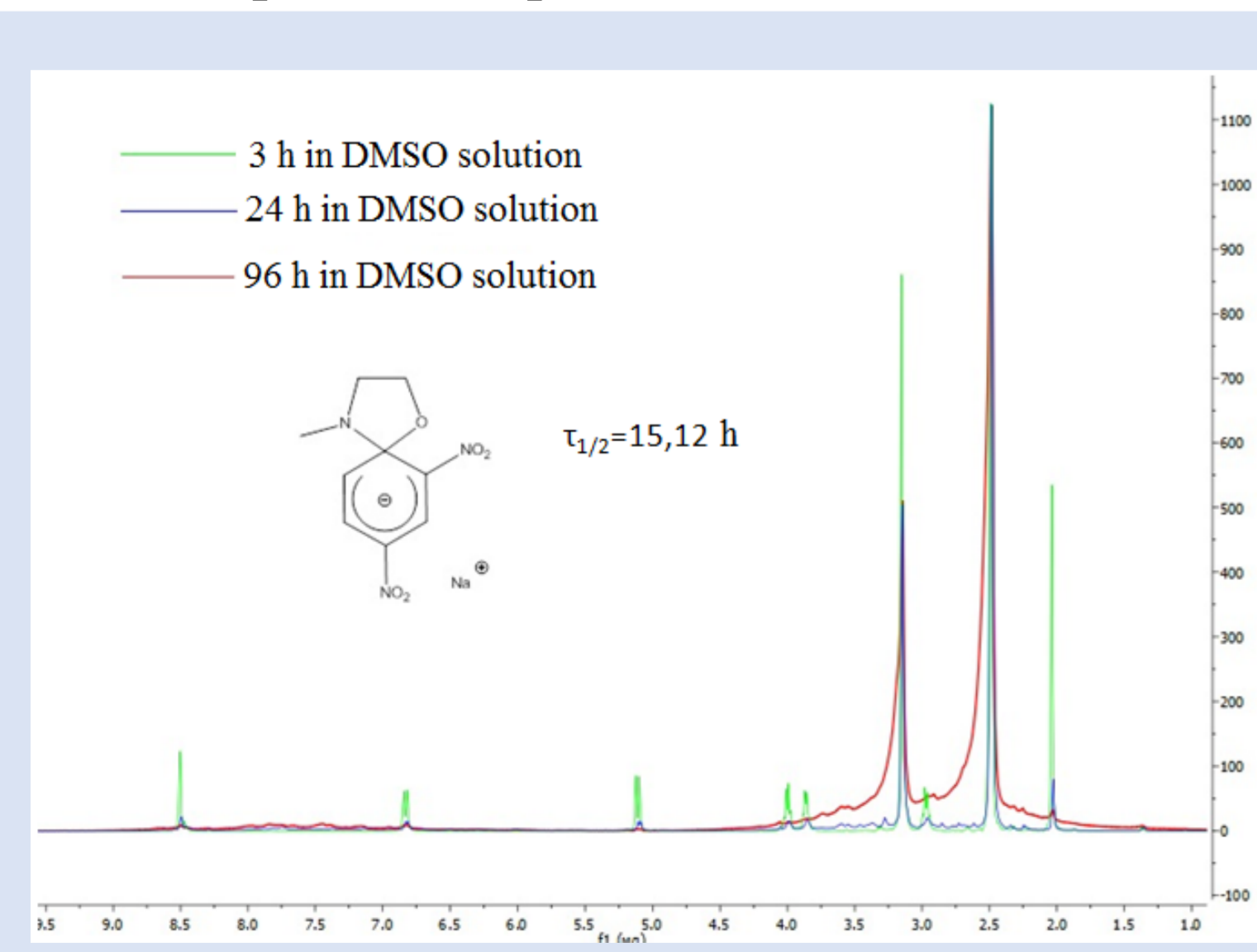

Fig. 3. Normalized UV-Vis absorption spectra of polymer composite films (**PCFs**) based on **PVB** doped with 50 wt. % Sp (*a*) and **NSp** (*b*).

The stability of the synthesized anionic σ-complexes was estimated by ^{1}H NMR (fig. 4) and UV-vis spectroscopy methods :

σ-Complex type	decay (half-life) constant, $\tau_{1/2}$, h
Sp (solution)	15,1 ± 0,1
Nsp (solution)	19,3± 0,1
Sp (in the solid PCF)	85,3 ± 0,1
NSp (in the PCF)	90,5 ± 0,1

Fig. 4. ^{1}H NMR spectra of Sp-complex in DMSO-d_6 solution after 3, 24 and 96 hours at room temperature (25 ^{0}C).

It was shown, that all studied film structures (in the sandwich structure type samples) exhibit photoconductivity effect under illumination by light from the synthesized anionic σ-complexes absorption region. The plots of electroconductivity (dark) j_d and photoconductivity current density j_{PH} on electric voltage U in double logarithmic coordinates can be approximated by straight lines, i.e. they can be described by the analytical dependences $j_d \sim U^{m_d}$ and $j_{PH} \sim U^{m_{ph}}$ used for the analysis of space-charge-limited currents in semiconductor materials. The dependence of j_{PH} on light intensity for all prepared PCFs is linear. Also the values of j_d and j_{PH} do not depend on the voltage sign.

It was shown that all obtained thin film structures are characterized by a high level of ionic conductivity (fig. 5).
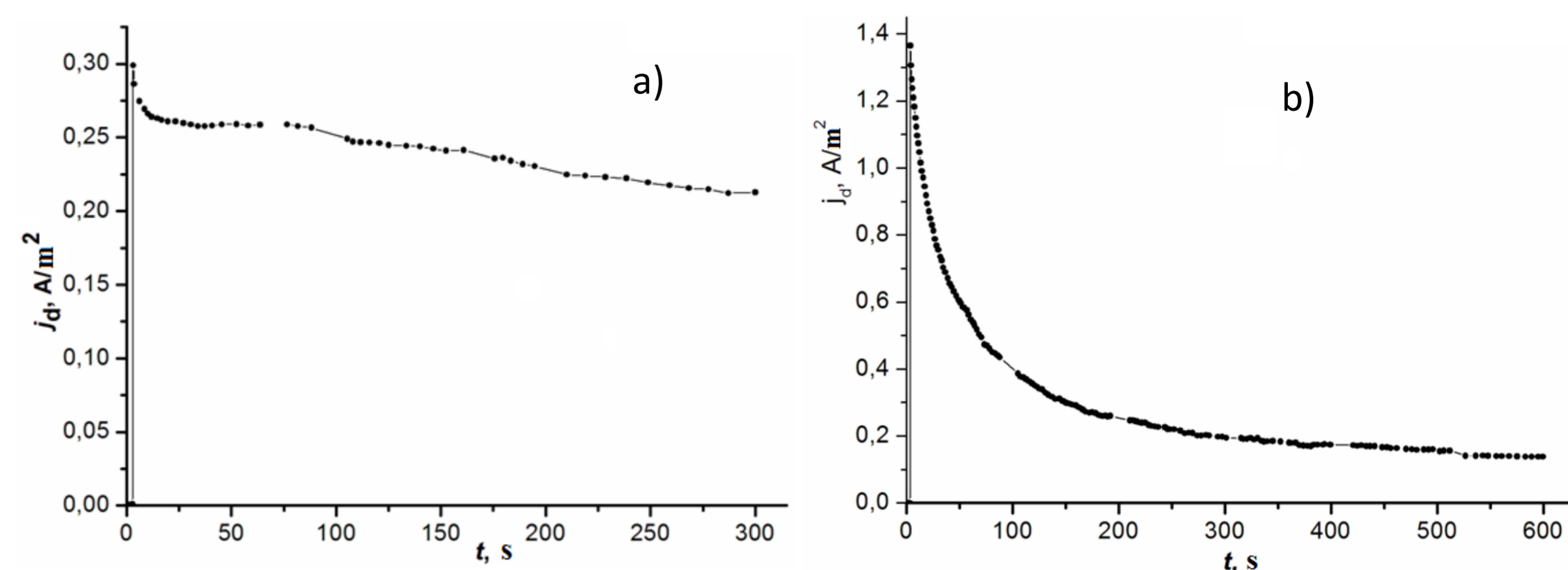

Fig. 5. Kinetics of the dark electroconductivity current density j_d in the sandwich structure samples of PCFs (ITO-PCF-Ag) doped with 50 wt.% the anionic σ-complexes Sp - **a**) and NSp – **b**) (electric field strength $E = 1{,}25 \cdot 10^7$ V/m).
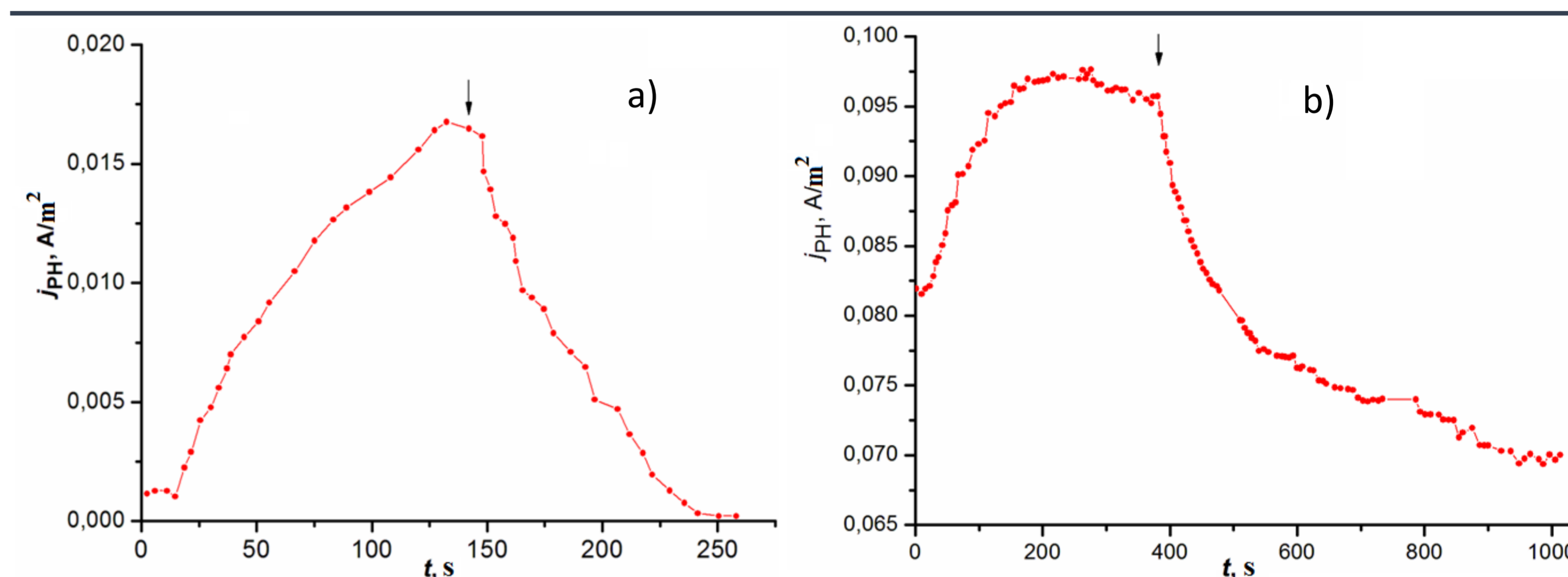

Fig. 6. Kinetics of the photocurrent density j_{PH} in the sandwich structure samples of PCFs based on PVB + 50 wt.% Sp - **a**) and PVB + 50 wt.% NSp - **b**), ($E = 1{,}25 \cdot 10^7$ V/m, the time moments of switching off the light illumination are shown by vertical arrows).

Photovoltage (surface) was measured by the modified Kelvin method in the samples with a free surface (under irradiation of the transparent ITO-electrode side). It was shown, that prepared film structures exhibit photovoltaic effect under illumination by light from the synthesized σ-complexes absorption region (fig. 7). It is suggested that observed in PCFs photovoltaic effect phenomenon is caused by the Dember effect, i.e. discovered effect has diffusion nature, because that the sign of the respective photovoltaic response V_{PH} becomes inverse under exciting light illumination of the different sides of irradiated samples. This fact confirms the correctness of our assumption about diffusion nature of the observed photovoltaic effect. In our systems case the potential of the non-irradiated (dark) surface becomes negative with respect to irradiated surface, because negative charged current carriers (electrons) have larger mobility. This confirms the n-type photoconductivity character of investigated PCFs.
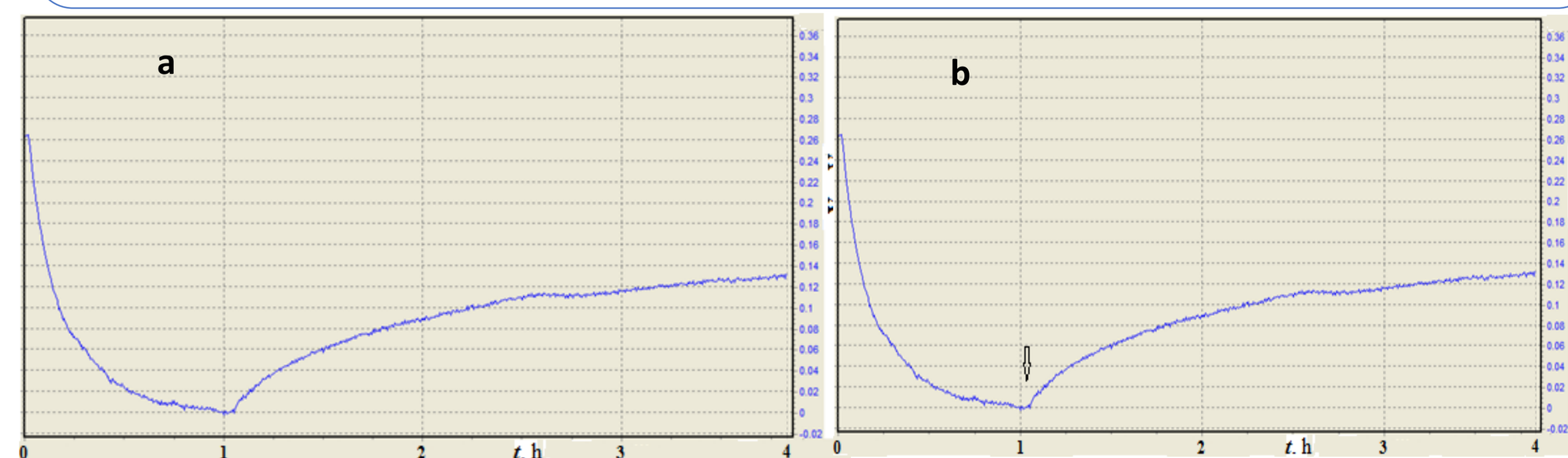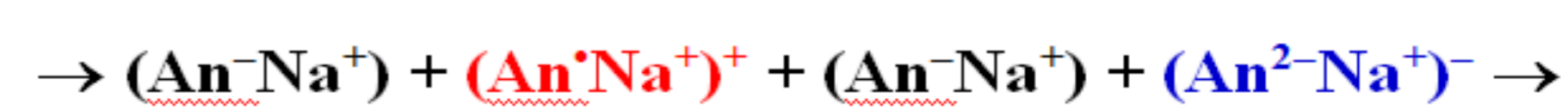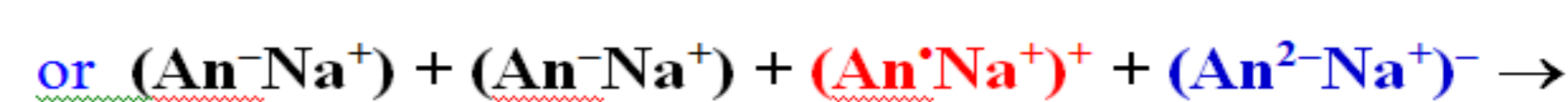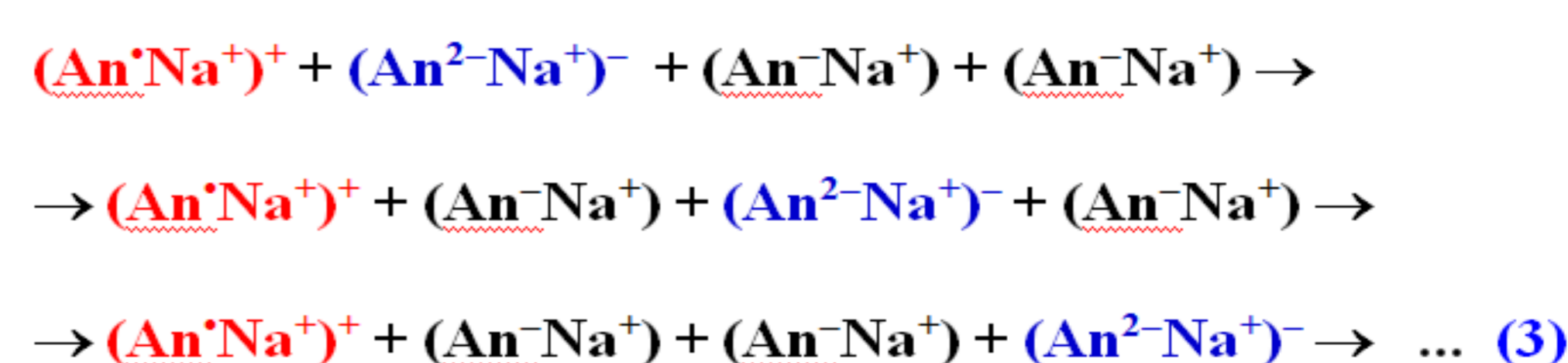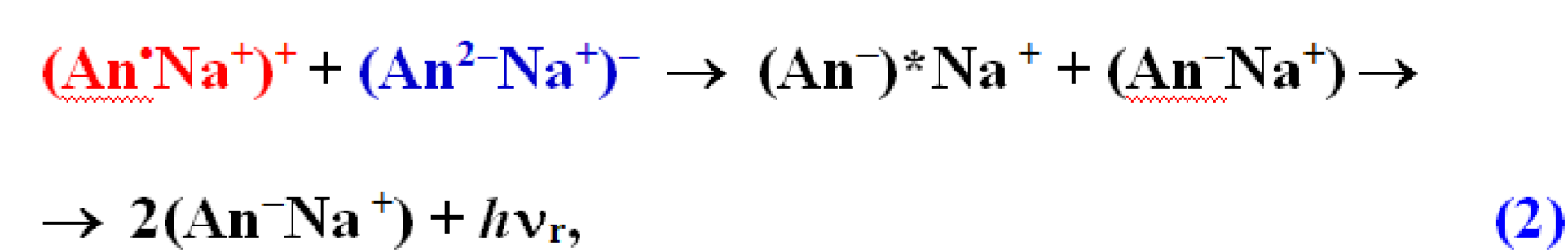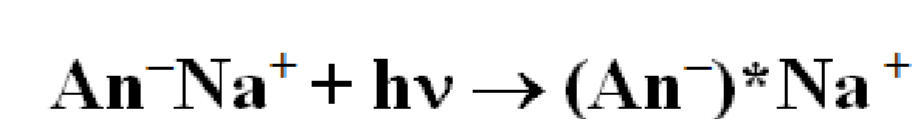

Fig. 7. Experimental oscillograms of the photovoltaic response V_{PH} in the PCFs based on PVB + 50% wt. NSp (**a**) and PVB + 50% wt. Sp (**b**). (λ_{irr} = 415 nm, I = 60 W/m^2). The time moments of switching off the light illumination are shown by vertical arrows.

Photogeneration schemes of non-equilibrium charge carriers in the PCFs with high concentration of anionic σ-complexes

$$An^-Na^+ + h\nu \rightarrow (An^-)^*Na^+$$

$$(An^-)^*Na^+ + (An^-Na^+) \rightarrow (An^\cdot Na^+)^+ + (An^{2-}Na^+)^- \rightarrow \quad (1)$$

$$(An^\cdot Na^+)^+ + (An^{2-}Na^+)^- \rightarrow (An^-)^*Na^+ + (An^-Na^+) \rightarrow$$

$$\rightarrow 2(An^-Na^+) + h\nu_r, \quad (2)$$

$$(An^\cdot Na^+)^+ + (An^{2-}Na^+)^- + (An^-Na^+) + (An^-Na^+) \rightarrow$$

$$\rightarrow (An^\cdot Na^+)^+ + (An^-Na^+) + (An^{2-}Na^+)^- + (An^-Na^+) \rightarrow$$

$$\rightarrow (An^\cdot Na^+)^+ + (An^-Na^+) + (An^-Na^+) + (An^{2-}Na^+)^- \rightarrow \quad ... \quad (3)$$

$$\text{or} \quad (An^-Na^+) + (An^-Na^+) + (An^\cdot Na^+)^+ + (An^{2-}Na^+)^- \rightarrow$$

$$\rightarrow (An^-Na^+) + (An^\cdot Na^+)^+ + (An^-Na^+) + (An^{2-}Na^+)^- \rightarrow$$

$$\rightarrow (An^\cdot Na^+)^+ + (An^-Na^+) + (An^-Na^+) + (An^{2-}Na^+)^- \rightarrow ... \quad (3')$$

Where 1 - Photogeneration, 2 - Recombination, 3,3' – Dissociation of geminate electron-hole pairs (EHP); An- - cyclic colored anion fragment of Sp or NSp.