

INTERNAL PHOTOEFFECT AND OTHER PHOTOELECTRIC AND SPECTRAL PROPERTIES OF FILM COMPOSITIONS BASED ON OLIGO-9-ANTHRACENYL GLYCIDYL ETHER DOPED WITH ANIONIC POLYMETHINE DYE



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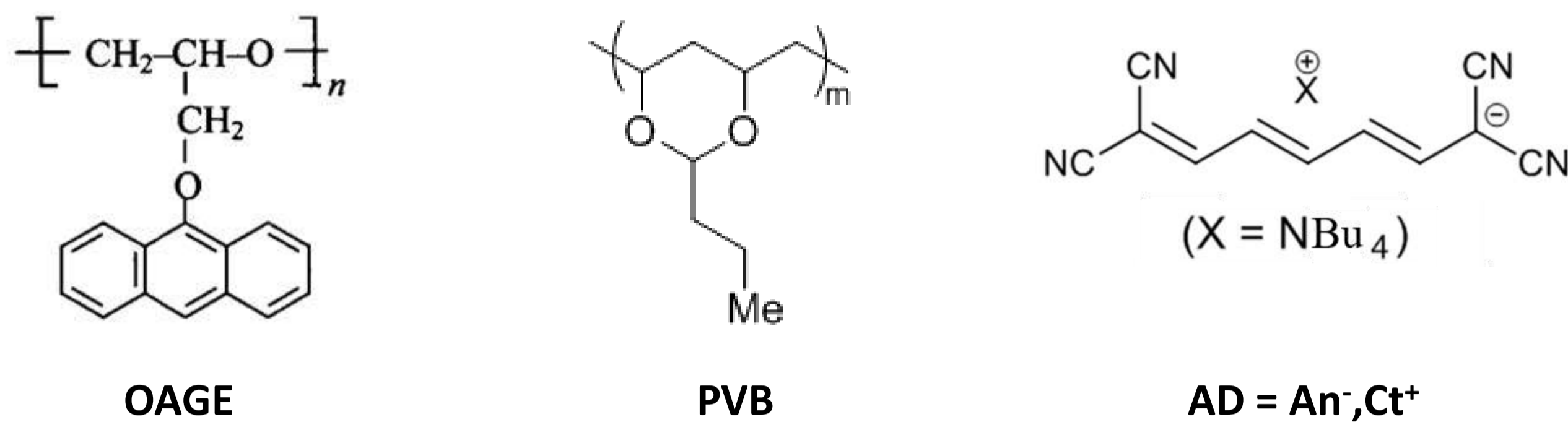
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Thin film polymeric compositions based on oligo-9-anthracenyl glycidyl ether (OAGE) doped with anionic polymethine dyes (AD) were prepared both with low and with high concentrations of dopant. Their spectral luminescent, and photoelectrophysical properties were investigated.

Photoluminescence quenching in an external electric field increases and a long-wavelength photoluminescence band and photoconductivity appear in the visible spectrum with increasing concentration of anionic polymethine dye in OAGE films. Associated species containing dye ion pairs are formed with increasing dye concentration. The kinetics found for the growth and relaxation of the photocurrent in these composite films is anomalous for photoconductor materials: the time required for growth of the photocurrent is much greater than the time for its relaxation after switching off the light. A prior irradiation memory effect of the films was discovered.

OBJECTS OF INVESTIGATION



RESULTS AND DISCUSSION

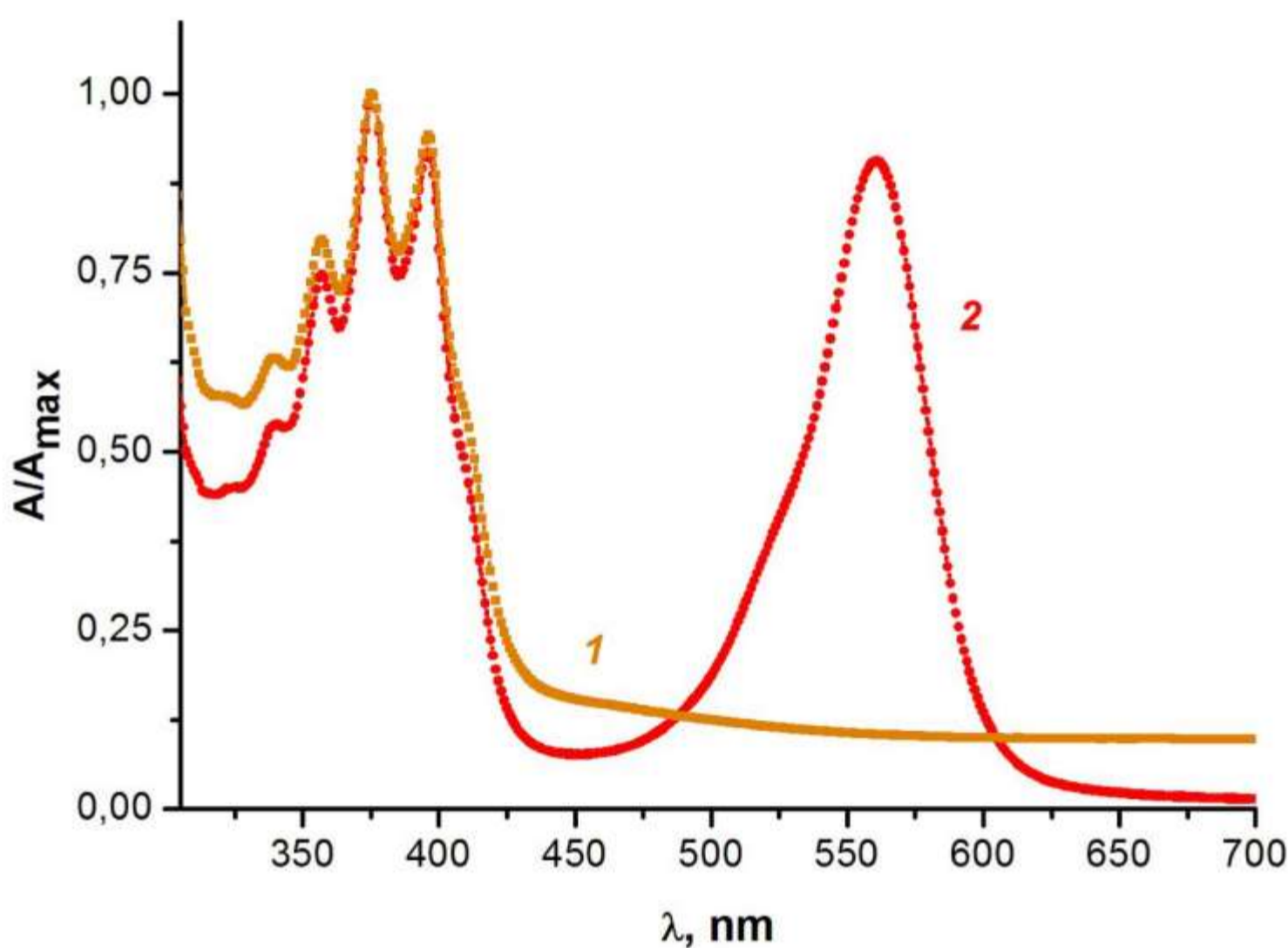


Fig. 1. Normalized absorption spectra of pure OAGE (1) and OAGE-based dye-doped (10 wt. %) (2) polymer composite films (PCFs).

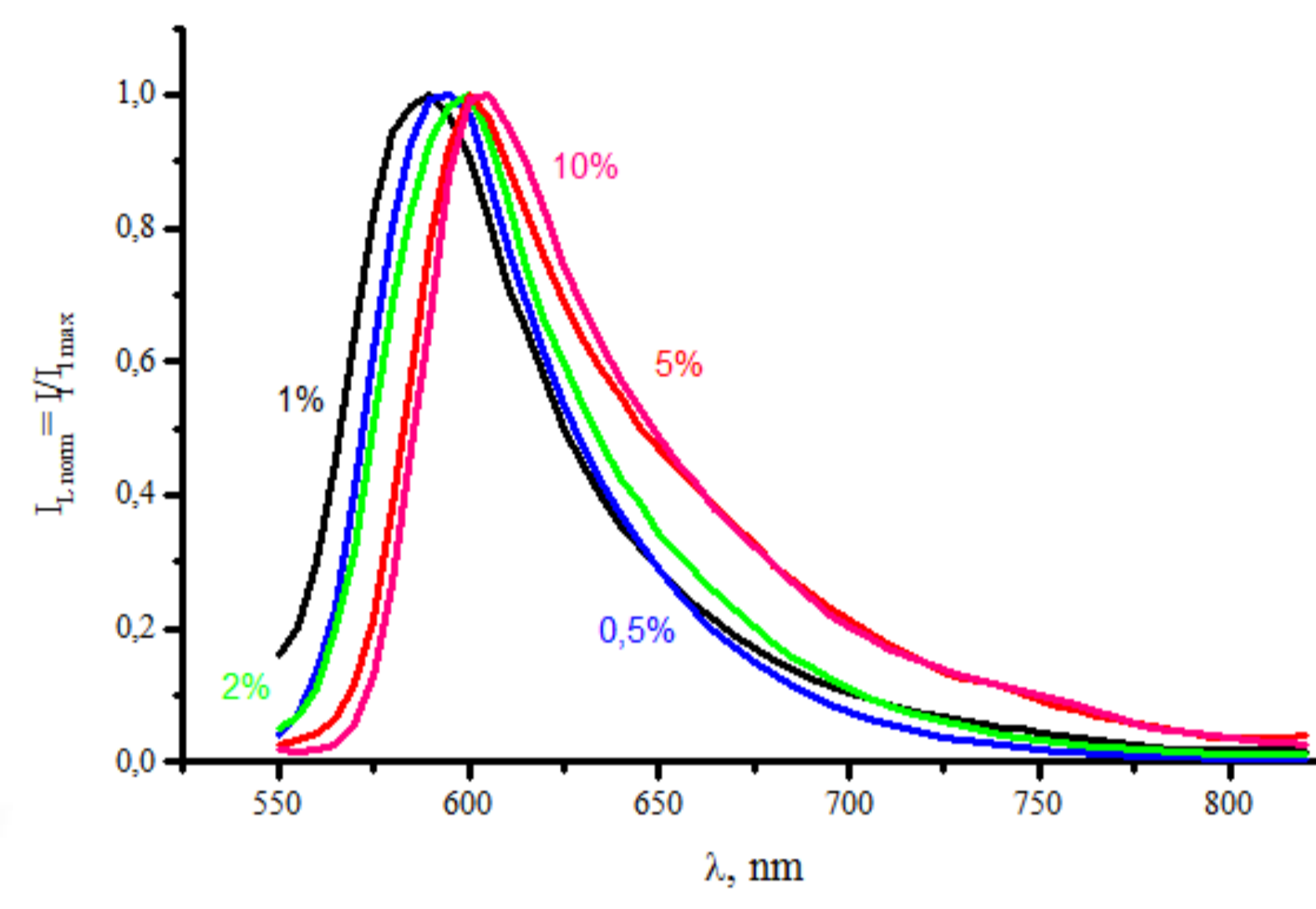


Fig. 2. Normalized fluorescence of the OAGE-based different concentration anionic dye-doped PCFs; λ_{ex} = 400 nm.

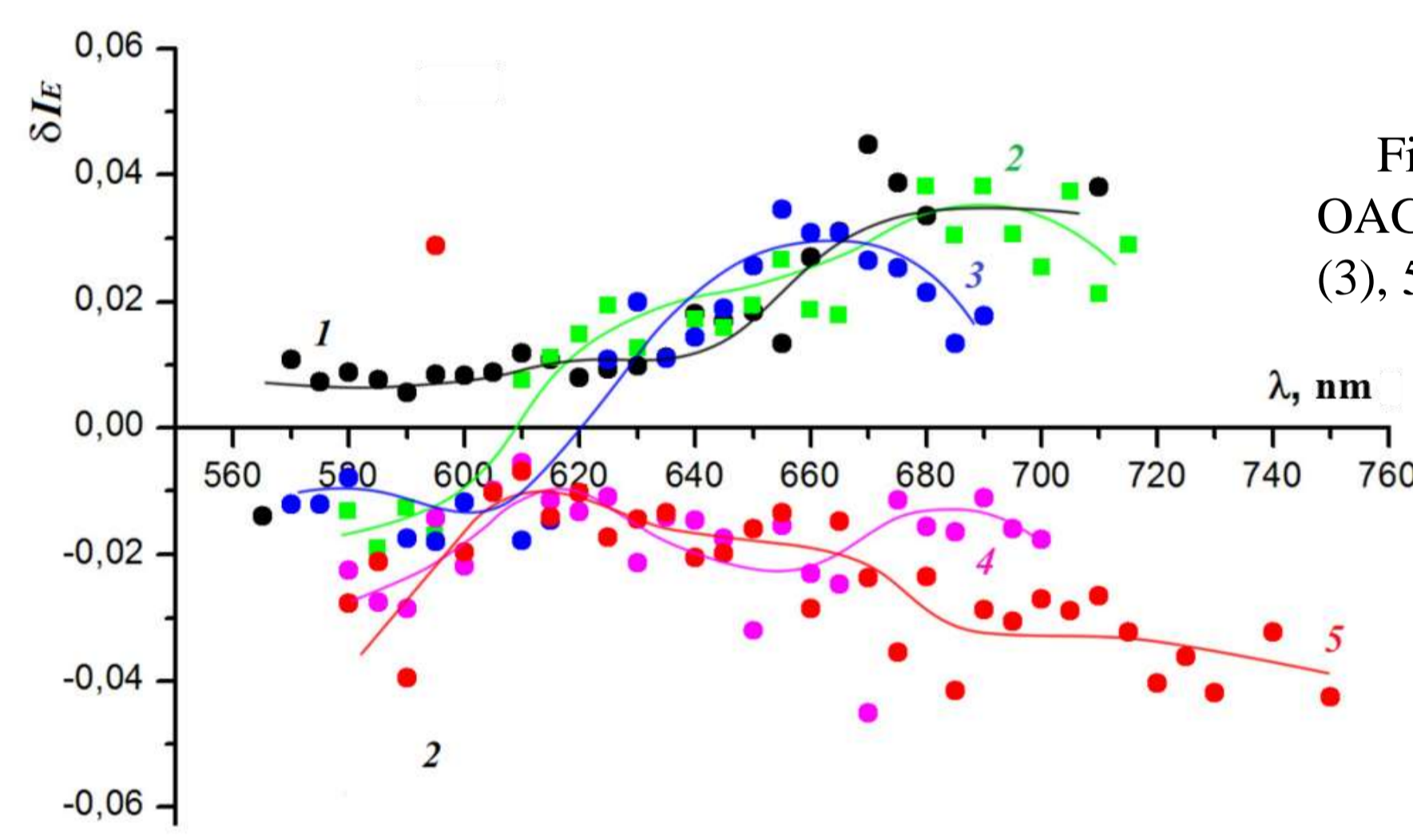


Fig. 3. Plot for δI_E vs. λ in PCFs derived from OAGE with AD concentration N = 0.5 (1), 1 (2), 2 (3), 5 (4), and 10 wt. % (5).

$$\delta I_E = (I_E - I_0)/I_E$$

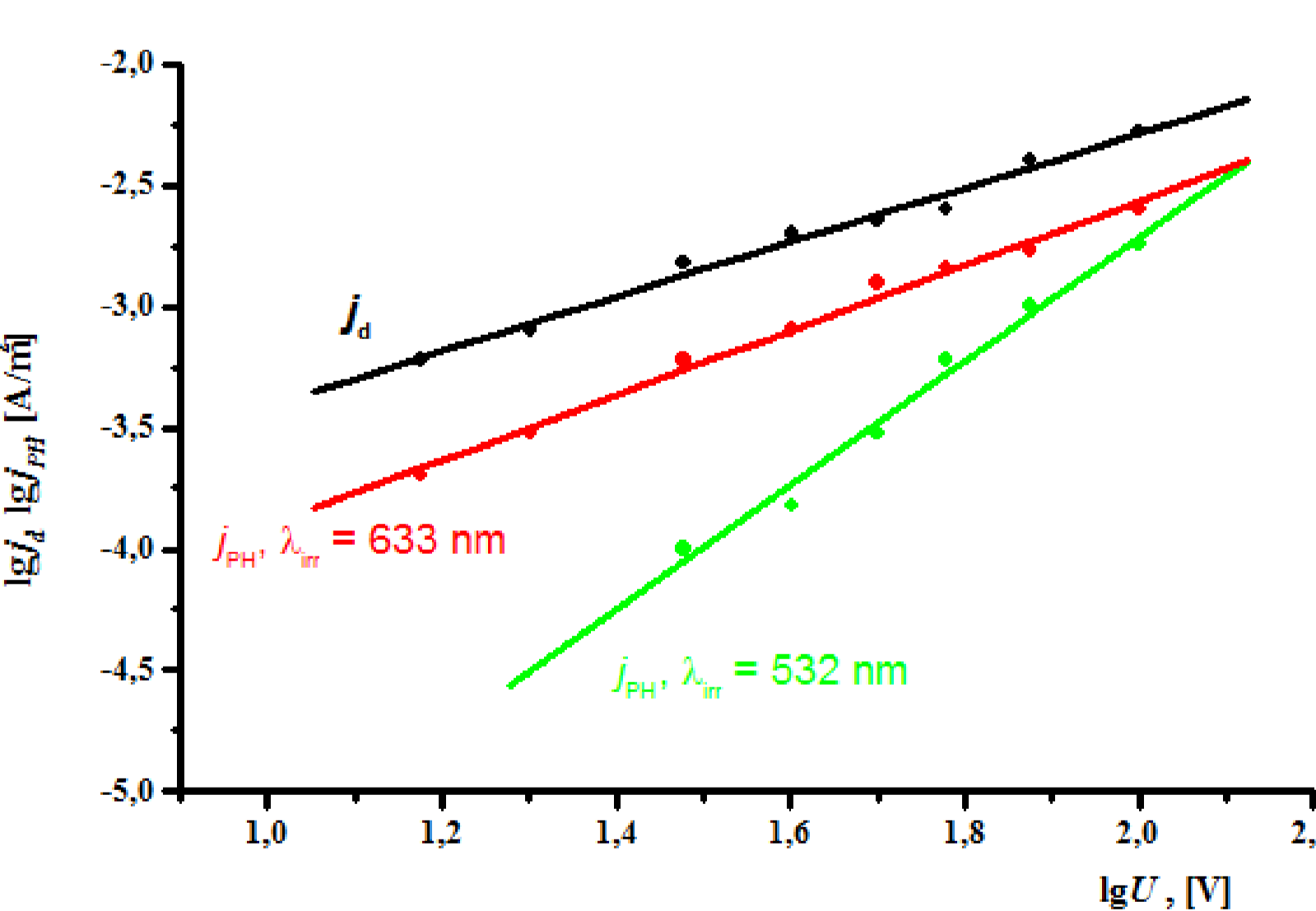
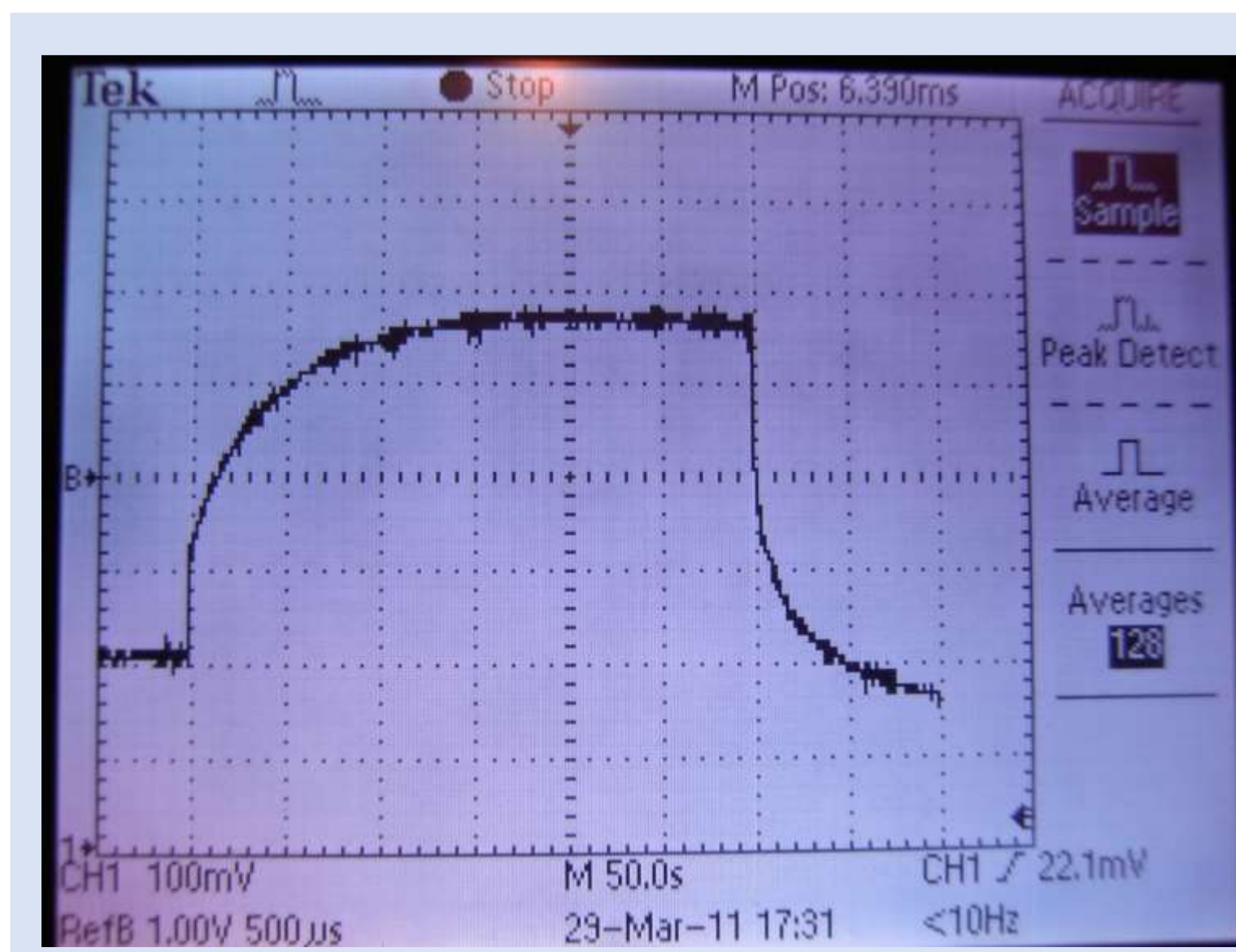


Fig. 4. Plots of lg(j_d) and lg(j_{PH}) on lg(U) in the sandwich structure samples of OAGE-based PCFs (ITO-PCF-Ag) doped with the anionic dye AD (N=10wt.%).

m _i	Value
m _d	1,1
m _{PH1} (λ _{irr} = 532 nm)	2,1
m _{PH2} (λ _{irr} = 633 nm)	1,4

The plots of j_d and j_{PH} on U in double logarithmic coordinates can be approximated by straight lines, i.e. they can be described by the analytical dependences j_d ~ U^{m_d} and j_{PH} ~ U^{m_{PH}} used for the analysis of space-charge-limited currents in semiconductor materials. The dependence of j_{PH} on light intensity both at λ_{irr}=633 nm and λ_{irr} = 532 nm is linear; this implies that the photoconductivity observed is not associated with a two-quantum processes. Also the values of j_d and j_{PH} do not depend on the voltage sign.

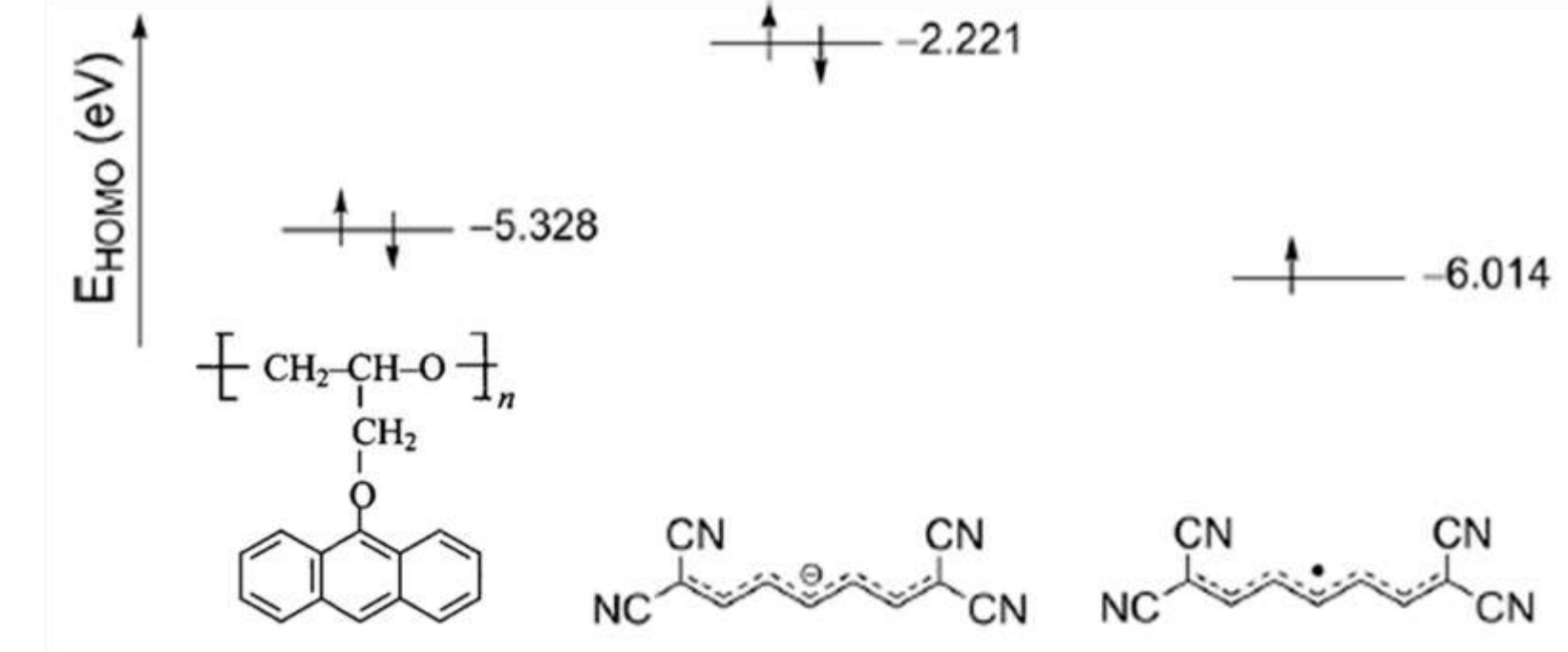


Unusual for semiconductor materials kinetics of the photocurrent growth and relaxation was observed in the films of these composites: photocurrent growth time is much longer than the time of its relaxation after the light is switched off.

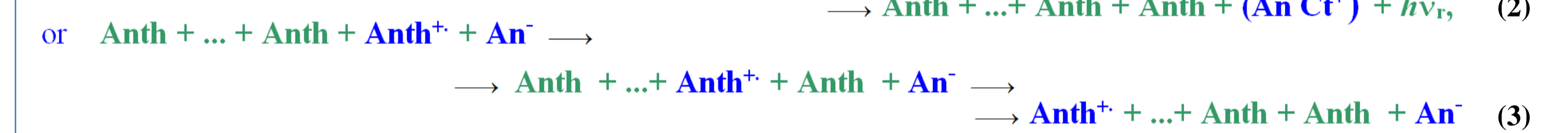
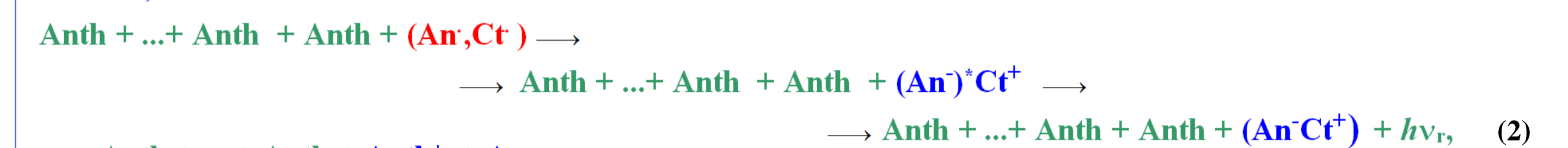
Fig. 5. Photograph of a anomalous kinetic oscillogram of the time dependence of the photocurrent j_{PH} under irradiation and after switching-off the light in the sandwich-structure ITO-OAGE + 10%wt. AD-Ag. Here, λ_{irr} = 633 nm and E = 51x10⁷ V/m.

Photogeneration schemes of non-equilibrium charge carriers in the OAGE PCFs with high concentration of anionic dye

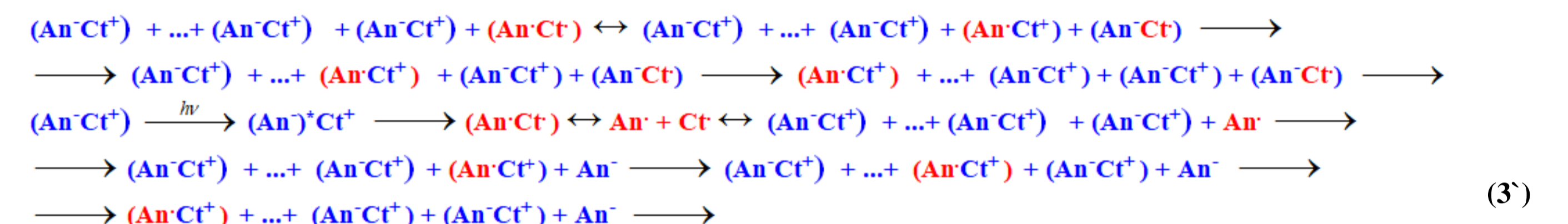
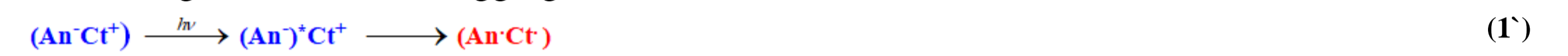
I. Photogeneration by electron transfer between the anthracene nuclei and photoexcited AD-aggregates.



II. Photogeneration with electron transfer to the counterion in the contact ion-pairs and OAGE:

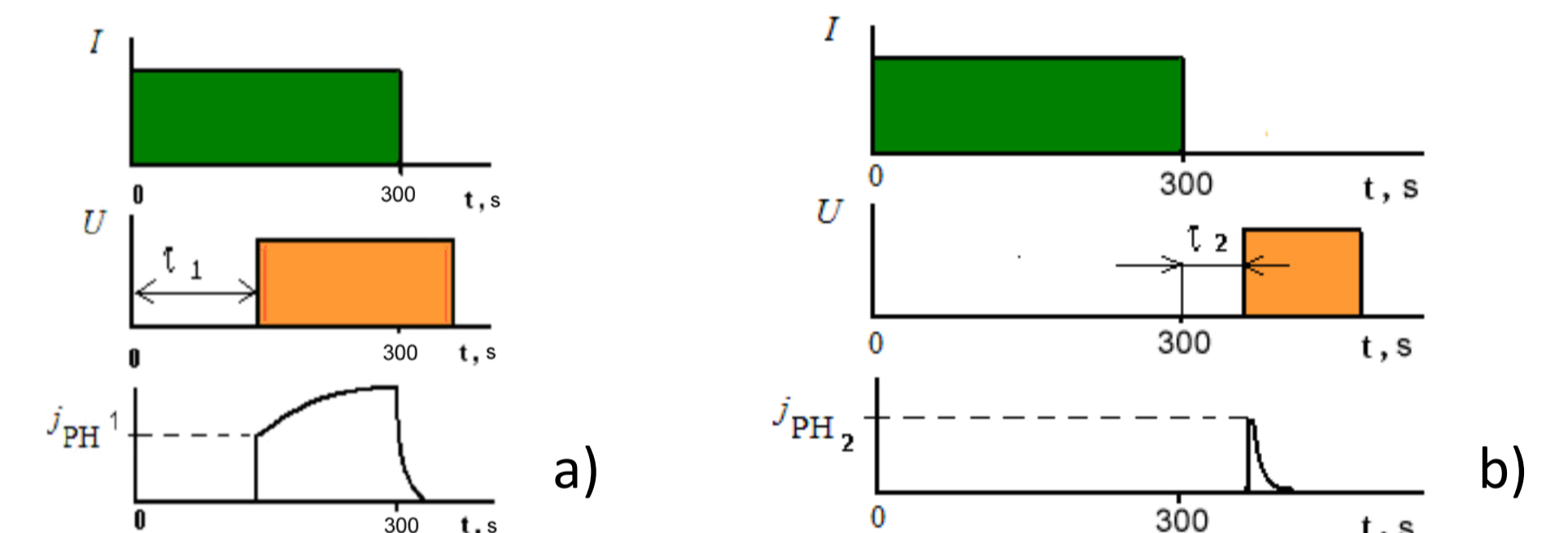


Photogeneration in AD-aggregates:



Where (1, 1') - Geminal Electron-Hole Pairs (EHP) Photogeneration, (2, 2') - EHP Recombination, (3, 3') - Geminal EHP Dissociation

A PRE-IRRADIATION MEMORY EFFECT OF THE OAGE-PCFs



Diagrams reflecting the method for: a) measuring j_{PH1} relative to the delay time τ₁ for application of an electric field after the onset of irradiation of the samples, b) measuring j_{PH2} relative to the delay time τ₂ for application of an electric field after switching off the light.

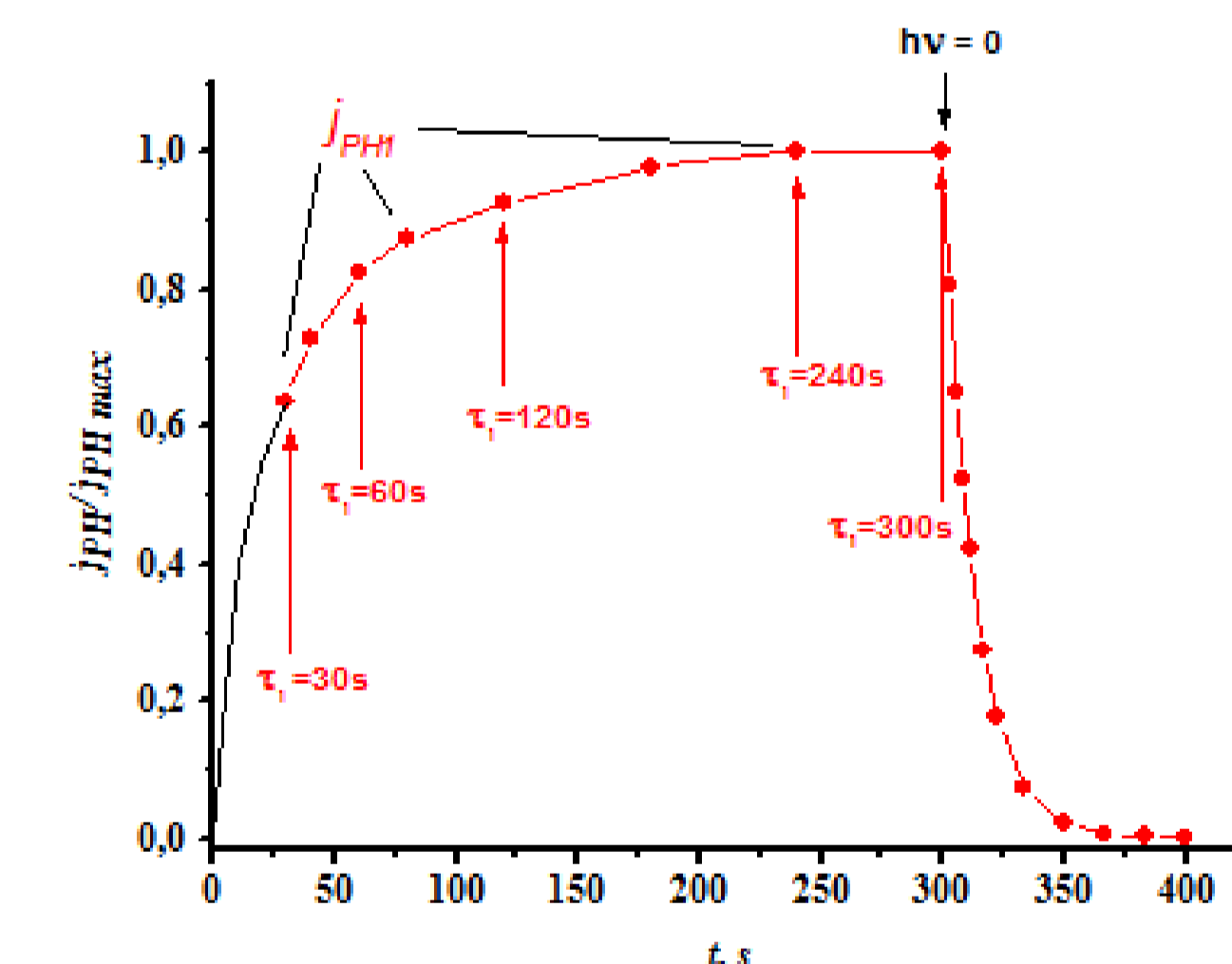


Fig. 6. Kinetics of the photocurrent j_{PH} and j_{PH1} for different τ₁.

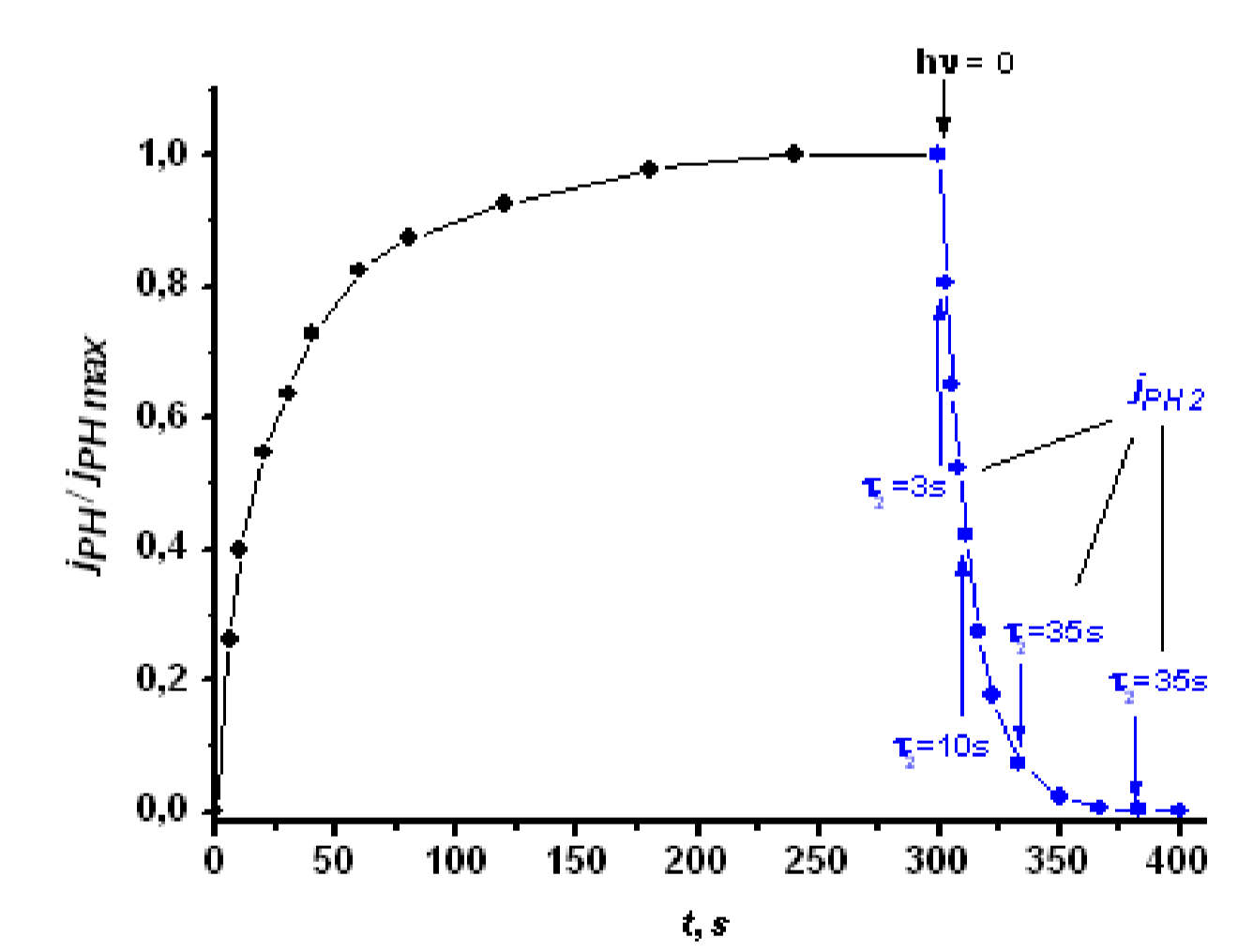


Fig. 7. Kinetics of the photocurrent j_{PH} and j_{PH2} for different τ₂.

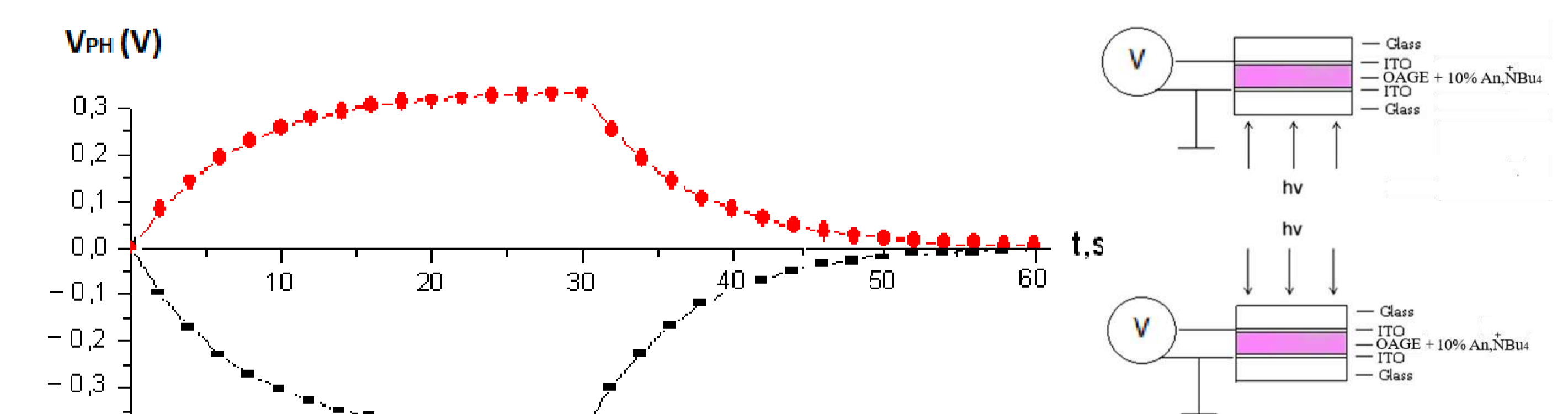


Fig. 8. Photovoltaic effect in the PCFs based on OAGE + 10% wt. AD. Measurements of the photovoltage value as a function of the angle of light incidence (varied from 0° to 180°) on the film showed that the response voltage exhibited sign inversion. This is evidence of the Dember mechanism of photovoltage generation.

It is known that an increase in the dipole moment (or in the concentration) of the polar dopant usually lowers charge carriers mobility. The observed in such PCFs unusual character of j_{PH} kinetics can be explained, possibly, by the light-induced long-living (since the electrostatic attractive forces disappear) neutral non-polar radical pairs (An⁻Ct⁺) accumulation in the system from polar anionic dye molecules (An⁻Ct⁺ ionic pairs) with non-zero dipole moments under light-irradiation according to Eq. (1, 1'). This can lead to PCF medium effective polarity decreasing and photogenerated charge carriers mobility increasing in accordance with the medium polarity decreasing respectively. Thus, the j_{PH} growth occurs under the "low" mobility conditions and, on the contrary, photocurrent relaxation occurs under the "high" mobility conditions and becomes faster. That causes the observed anomalous character of respective photocurrent growth and relaxation kinetics. The significant photoinduced accumulation of long-lived charged electron-hole or neutral radical pairs in the PCFs with the high dye concentration also confirmed by the fact that under long-time light illumination (~ 30 min, I = 50 W/m²) of such samples (in the dye absorption region) the very slow reversible discoloration process of illuminated films occurs even without applying an external voltage.