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Electrical conduction mechanism in *N*-(*p*-R-phenacyl)-4,5-diazafluorenium-9-one bromides thin films

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Abstract

The synthesis and the study of temperature dependence of the electrical conductivity, σ, and Seebeck coefficient, S, for some new organic salts, *N*-(*p*-R-phenacyl)-4,5-diazafluorenium-9-one bromides, in thin films, is reported.

The dependences $\ln\sigma(10^3/T)$ and $S(10^3/T)$ are typical for p-type semiconducting compounds. The values of some characteristic parameters for the examined compounds (the thermal activation energy of electrical conduction, ΔE, the ratio of carrier mobilities, b, etc.) have been determined. The obtained values of ΔE ranged from 1.71 and 2.01 eV, while those of b lay in the range 0.70–0.87. The analysis of the absorption edge evidenced direct energy gaps, ranged between 3.31 and 3.39 eV, as well the presence of Urbach absorption tails.

Some correlations between respective values and molecular configurations of the present organic salts are established. The model based on band gap representation is suitable for the explanation of the electronic transfer mechanism in the investigated compounds.
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1. Introduction

Organic semiconducting compounds are a new class of electronic materials, considered as perspective materials for low cost organic electronics [1,2].

During the last two decades, they have attracted considerable attention of scientists working in both fundamental (approach of problems concerning the nature of charge transfer) and applied research.

Thanks to their well-known suitability to 'molecular tailoring', at present, the number of registered synthesized organic compounds exceeds 17 million [3].

Organic semiconductors combine novel semiconducting electronic properties, which can be tuned by modifying their molecular structure, with high processability, which make them very versatile and suitable for an important number of large area applications. Own to their efficient electroluminescence, band gap in the IR–vis range, high mobilities of charge carriers, they are promising candidates for the technology of solid-state electronic devices (the new low cost 'plastic' electronics): field-effect transistors, light-emitting diodes, lasers, photovoltaic cells, etc. [4–10].

Organic compounds in thin films are generally characterized by weak London-Van der Waals intermolecular bonds, which result in comparatively poor self-organizing properties, therefore their structure and electronic properties are strongly dependent on the deposition technology.

In a series of previous papers [11–17], we have investigated the electronic transport properties (both electrical conductivity and Seebeck coefficient, in dependence of temperature) for an important number of new organic compounds, revealing semiconducting behavior.

In present paper, we report on the synthesis of four new organic salts, namely *N*-(*p*-R-phenacyl)-4,5-diazafluorenium-9-one bromides, and study the electronic transfer mechanism in thin films of respective compounds.

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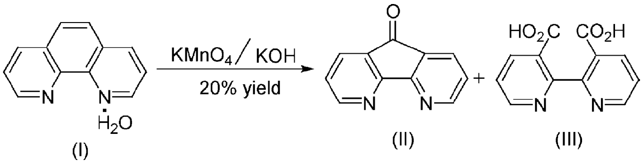
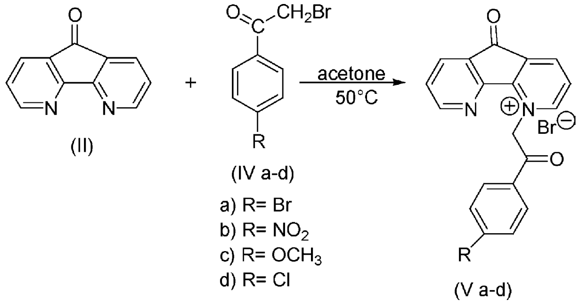
2. Experimental

2.1. Synthesis of compounds

4,5-Diazafluoren-9-one (II) has been synthesized by oxidation of 1,10-phenanthroline (I) with alkaline potassium permanganate, yielding 2,2′-bipyridil-3,3′-dicarboxilic (III) acid from which it was easily separated [18].



There were obtained four new monoquaternary salts derivated from 4,5-diazafluoren-9-one by Krohnke method [19,20]. Thus, *N*-(*p*-R-phenacyl)-4,5-diazafluorenium-9-one bromides (V) have been prepared with good yields (70–90%) by reaction of 4,5-diazafluoren-9-one with 2-bromo-4′-R-acetophenones (IV). The reaction was carried out in a minimal amount of anhydrous acetone at soft heating (50 °C) and a small excess of reactive halides was used.



The obtained compound have a yellow color and they are soluble in water, ethanol, methanol, dimethylsulfoxide, acetonitril, *N*,*N*-dimethylformamide and insoluble in ether, acetone, and chloroform. The resulting salts have been isolated by filtration and purified by recrystalization from an appropriate organic solvent.

The compounds RA1–RA4 (Table 1) were finally obtained as polycrystalline powders. Their molecular structure was confirmed by elemental and spectral (IR, ^{1}H NMR) analyses.

2.2. Study of the electronic transfer and optical properties

In order to study the electrical, thermoelectrical and optical properties of respective organic compounds thin films were deposited by using an isothermal immersion technique (deposition from the solution) [11,13,21] onto glass substrates, maintained at room temperature. Ethanol was used as a solvent.

The electrical measurements, i.e. temperature dependences of electrical conductivity and Seebeck coefficient, were performed by using surface-type cells [13,22].

Table 1
The substituents R in the molecular structure of present organic salts

Compound	RA1	RA2	RA3	RA4
–R	–Br	$–NO_2$	$–OCH_3$	–Cl

Thin silver and indium films ($d \approx 1$ μm), deposited onto the substrates by vacuum evaporation before the organic film deposition, were used as electrodes. They were separated by a gap of 8–15 mm. In all cases, low electric fields (with an intensity of under $100\ \mathrm{V\,cm^{-1}}$) were applied, so that non-ohmic effects have not been registered.

The film thickness, as measured by an interferometric method, lay in the range 0.51–2.00 μm.

The surface morphology of investigated compounds was examined by AFM technique.

The experimental arrangements used for the study of electrical properties were similar to those described in [11,13,23].

In measuring the thermoelectric effect, sonde electrodes maintained at a temperature difference $\Delta T = T_2 - T_1$ equal to 10–12 K, were used. The Seebeck coefficient, *S*, was determined by means of following relation [13,24,25]:

$$S(T) = \frac{V_S}{\Delta T}, \tag{1}$$

where V_S is the Seebeck voltage, measured with a Keithley 6517A electrometer, and $T = (T_1 + T_2)/2$ is the temperature to whom *S* corresponds.

In studying the optical properties of organic salts, the transmission spectra, in the range 1.60–3.60 eV, have been recorded with a SPECORD M-40 spectrophotometer (Carl Zeiss, Jena).

The absorption coefficient, α was determined by means of the expression [26]:

$$\alpha = \frac{1}{d}\ln\left(\frac{I_0}{I}\right), \tag{2}$$

where d is the film thickness, I_0 and I denote the intensity of incident and emergent beam, respectively. The use of the approximate formula (2), which does not include the reflection correction, is rightful in the present case, where for photon energies, $h\nu$, less than E_g (the energy gap), the reflection factor of sample surface, R, is comparatively small (under 10%).

3. Results and discussion

The structural investigations evidenced a prevailing polycrystalline (granular) structure of present films. The film structure is seen to depend on compound nature, as well as film thickness. As indicates AFM inspection (Fig. 1), the microstructure is typically polycrystalline, continuous and pinhole-free.

Our experiments showed that the temperature dependence of the electrical conductivity, σ, of organic films, obeys the well-known law [25,27,28]:

$$\sigma = \sigma_0 \exp\left(\frac{-\Delta E}{2kT}\right), \tag{3}$$

where ΔE represents the thermal activation energy of the electrical conduction, T is the sample (absolute) temperature, k is the Boltzmann’s constant, and σ_0 denotes a parameter depending on the semiconductor nature.

Our studies revealed that the law [3] is valid for a large number of organic compounds with similar chemical structure [11–17].

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