Analysis of thermally stimulated processes in new phenanthroline derivatives suitable for optoelectronic devices

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Abstract. Thermally stimulated processes have been studied in thin films of phenanthroline derivatives to describe the states that had been localized. Ultraviolet Photoelectron Spectroscopy had checked out before thin films of new pyrrolo[1,2-a][1,10] phenanthroline derivatives [1], in order for further applications in optoelectronic devices. The investigated compounds have an electronic band structure which is due to the substituent (R=NO2, Cl) induced transformations of molecular orbitals. Thermally stimulated discharge currents (TSDC) attested dipolar and charge transport mechanisms. Each TSDC peak has been assigned to elementary processes that are different utilizing in addition dielectric spectroscopy (DES), and the mean trap depths have been approximated from thermally stimulated luminescence (TSL) curves.

1. Introduction
The candidates that are promising for the technology of solid-state devices, organic light emitting diodes (OLEDs) [1] in particular, are the Pyrrolo[1,2-a][1,10]phenanthroline (RA) derivatives. Due to their ionization potential and electron affinity, the above-mentioned materials are captivating for the optoelectronic devices, allowing electron injection at the cathode [2,3]. Because of the specific chemical structures of these materials, molecular orbitals can be tuned by inserting acceptor or donor groups, obtaining emissive or electron transporting/hole blocking materials [4].

The mix between the hole transporting materials like polyparaphenylenevinylene (PPV), and pyrrolo[1,2-a][1,10]phenanthroline as electron transporting in hetero-layer structures is a technique to develop new performances of OLEDs in contrast with single layer diodes. The requirement of finding and describing new materials suitable as charge transporting layers in OLEDs is critical from this perspective. Electronic processes in phenanthroline derivatives have been studied, and then, the localized states [5-7] have been examined by utilizing the thermally stimulated techniques. The basic valence electronic structure was given by the UPS measurements, while the electronic transport processes in bulk materials [8] have been described by the thermally stimulated techniques (TSDC, TSL) and impedance spectroscopy (DES). For a better quality of these devices, the attention needs to be distributed to materials synthesis and to the study of the electronic structures of these devices which allows apprehending of their conduct in organic electronic devices [9]. On the other hand, the continuous decrease in fabrication size leads to a significant increase in the effects of thermally induced / assisted phenomena which should be carefully addressed [10].

The chemical structure of pyrrolo[1,2-a][1,10]phenanthroline derivatives is presented in Fig. 1. [11-14]. By spin coating, the thin films were placed in clean conditions and onto flat silicon. The
thickness of the film determined from the ellipsometric measurements was 100 nm for the study samples. We utilized a toroidal grating monochromator (TGM2-beam line) covering the photon energy range from 5 to 190 eV. At the room temperature [1], the photoelectrons were gathered with an ADES 400 angle resolving spectrometer system. During the experiment, performed at BESSY (Berlin) [1], the base pressure was 2 x 10-10 mbar.

![Chemical structure of pyrrolo[1,2-a][1,10]phenanthroline derivatives investigated](image)

RA1: R=NO2, R1=R2=COOCH3
RA2: R=Cl, R1=R2=COOCH3

Figure 1. Chemical structure of pyrrolo[1,2-a][1,10]phenanthroline derivatives investigated

The photoelectron spectra were measured at an incidence angle of 450, in normal emission, for incident energies 50 eV. By utilizing solution-casting technique, thermally stimulated analysis samples were prepared: polymer films were cast on the surface of freshly evaporated aluminum copper (RA) from a chloroform solution, allowing the solvent to evaporate slowly. We heated the films up to 360 k for 10 hours, and then, to eliminate any residual solvent, dried them in high vacuum (5 x 10-6 Torr) for 2 hour at Tg, gained using a constant heating rate of 0.5 K/s. All measurements were made with a custom configuration [2]. With a temperature range between 75 and 450 K, we performed the TSL measurements. We used a 1000 W Xenon lamp as an excitation source and, at a constant temperature, we illuminated the samples for 15 min, and, after we switched off the light, we heated them with a linear rate of 0.1 K/s. Evaporating a second aluminum electrode (150 nm) under UHV conditions [2], we utilized a sandwich configuration in order to achieve TSDC and DES measurements.

2. Results and discussions

UPS spectra of compounds RA1(a) and RA2(b) is being shown by Figs. 2. Also, the same figures show the theoretical simulations for different incident photon energies of both compounds. The vacuum level (E0) has been set at zero [15], and all energy values were considered in respect with it. The incident photon energy used for the measurements presented in Fig. 2, was 50eV. For clarity, we used vertical offsets. Between experimental findings and theoretical results, a good agreement had been found, and, through this, each UPS peak has related to the specific contributions of distinct groups of occupied molecular orbitals [15-18]. A good agreement between experimental findings and theoretical results was found, allowing relate each UPS peak to the specific contributions of distinct groups of occupied molecular orbitals [15-18]. Due to the highest occupied molecular orbital (HOMO level), the lowest binding energy peak is essentially for both compounds. Also, the π-orbitals produce this emission. For compound RA1, the first peak has its onset at 2.11eV, in case of 50eV incident photon energy. For compound RA2, its onset is at 5.60eV, in case of 50eV incident photon energy. The mixture between π- and σ- states The second peak is already due to a mixture of π- and σ- states. The other peaks are related to two and three centers σ-states. As it can be seen in Fig 2, The HOMO’s energy positions is As it is presented in Fig. 2, the HOMO’s energy positions and of very close states do not practically change in examined compounds; therefore we can assume that there is not any shift with the molecular size [17, 18].

We will now take a closer look at the obtained spectra. When we increase the exciting energy from 40eV to 50eV, the beam electron density is strongly intensified for both compounds, due to the interaction between molecular electrons and photons for deeper orbitals that has an increased probability. In the case of compound RA1(R=NO2), at 50 eV - excitation electrons from the orbitals
previously excited at 40 eV are also emitted, but the latter are occupied by electrons emitted from the deepest orbital. In this way, at 50eV-excitation the levels by 2.90 eV and 9.66 eV are poorly evidenced. The highest localized orbital is the localized orbital by 2.90 eV. This localized orbital forms at the absorption band’s long wavelength limit. A rather wide band with maximum at 7.36 eV can be observed because of the bands’ overlapping at 5.00 eV, 9.66 eV and 6.60 eV, and because of the electronic background from the deepest orbital (by 23.31 eV), at 50 eV incident energy. For compound RA2 (R=Cl), the 1.85 eV, 3.80 eV and 5.55 eV levels are not observed due to the same reason. This threshold is seen to displace toward small energies because of overlap with the intense band from 5.55 eV. Further present at 8.72 eV and 10.72 eV are the characteristic bands of Cl. The weak band located at 12.90 eV is further present as well. Due to the deepest orbital, the increase of current density is over 15eV. The increase can be observed at exciting energies. We improved TSD, TSL and DES measurements to describe the localized states. TSDC spectra of RA1 and RA2 are shown in Fig. 3. Spectra of RA1 and RA2 show two peaks. Both can have a dipolar origin or both can return from charge transport processes.

![Figure 2](image-url) UPS valence band spectra of compounds RA1 (a) and RA2 (b) at 50 eV incident photon energy.

The DES measurements were carried out on both types of RA to inspect their nature. In figure 4, we can see exemplified the DES spectra for peaks II and I in RA2. As it is shown, in peak I is no evidence of any evidence of dipolar relaxation, which is very clear instead for peak II. On one hand, the scanned temperature range was established by presuming a single elementary relaxation process, and taking into account the connection between the relaxation frequency [20] and the TSD current. The single elementary relaxation process can be found described by an Arrhenius law. On the other hand, the scanned temperature range was established by using the Debye description [21-23] of the dielectric constant complex component [18, 22, 23].

Both of the peaks have different nature. While peak II has dipolar origin, peak I may be due to charge transport processes, and particularly to trap states in the material. The TSL measurements have been consequently performed to investigate the presence of the trap distributions. In Fig. 5, the resultant TSL curves for RA1 and RA2 are shown. According to Halperin and Braner [21], and based on the mean activation energy, Ea, utilizing Lushchik’s formula [21-23], the symmetry factor $\mu_g$ has been estimated. In Figure 5 it can be observed the obtained values. Two trap states have been showed by all materials: for RA1 and RA 2, a shallow one at 0.14 eV, and for RA2, a deeper state at 0.24
eV. We cannot determine if the carriers are holes, electrons or both, based only on these TSL results, but there is a chance to estimate the trap densities [23].

![Graph showing TSDC spectra of RA1 and RA2](image)

**Figure 3.** TSDC spectra of RA1 and RA2

![Graph showing DES spectra peak I and peak II for RA2](image)

**Figure 4.** DES spectra peak I and peak II for RA2

3. Conclusion
The UPS measurements were carried out in two different types of pyrrolo[1,2-a][1,10]phenanthroline derivatives, to induce their valence band structure, and their respective potentials of ionization. We obtained a good agreement between the experimental curves and the quantum chemical simulations of UPS spectra. This agreement suggested that the calculated dipole moments are reliable. To describe the localized states, the TSDC, DES and TSL measurements were carried out that present the existence
of dipolar relaxation and charge transport processes because of the trap states. The trap states that are large enough are the deeper trap states, and they can contribute to the carrier transport in OLEDs.

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