IPID4all Doctorate Research Exchange with Vrje Universiteit Amsterdam
Feedback report

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Exchange topic: *Investigation of the structure-function relationships in conjugated small molecules liquid crystal dyes, for their application in organic electronic*

Introduction

Organic semiconductors are known over decades now, to be a very promising technology for energy production, as well as for the photonic and optoelectronic industry. Nevertheless, organic semiconductors show in general much disordered transport, in comparison to their inorganic counterparts [1-2], which means much lower carrier mobilities, limiting their efficiency and life time while processing them inside devices. Therefore, materials which offer much better control over their thin film structure are for high interest, to achieve that goal of high performance organic electronic. In this respect, liquid crystals (LC) semiconductors known to have unique structural characteristics which can be controlled via electric fields or temperature, appear then to be a great alternative. In the scope of my PhD project, which this research stay was a part of, the charge transport properties in newly synthesized soluble liquid crystalline dyes are investigated. To address the question of the limitation of mobility arose above, the LC properties of the new materials namely, their self-assembly, high thermal stability and ambipolarity, are exploited to improve transport properties. We aim to add insights, in the understanding of structure-property relationships in LC semiconductors, for improvement of transport properties in organic semiconductors.

In the scope of this research stay, the structure-function relationships in two novels liquid crystal dyes which exhibit pretty similar chemical structures, but show a big difference in their Mesophase, were investigated through experimental characterizations. Namely, electrical characterizations using current-voltage and impedance spectroscopy have been used to study the charge transport properties of these two materials, while optical characterizations (Raman spectroscopy and transient absorption) were used to investigate structural difference amongst these two materials.

Research Undertaken

The overview of results obtained are summed up below. And before discussing them, we would like to mention that for the reason of confidential agreement within us and the industrial partner concerning the materials, these ones will be designated for the moment only by their code names: IS-19452 and IS-19507, and their chemical structure will not be displayed.

Properties of the materials

The conjugated LC dye IS-19452 presents two phases depending on the temperature treatment of the film, respectively: a crystalline (**C**) and isotropic phase (**I**). The LC dye IS-19507 presents four different phases namely: a crystalline, two smectic (**Sm**) and an isotropic phase.

The phase transition sequences for both is shown below:

IS-19452: C 131 **I** **IS-19507: C** 116 **Sm?** (103) **Sm?** 141 **I**

All films in these studies were prepared from chloroform (CHCl3) solution with a concentration of 15 mg/mL and 20 mg/mL depending on the process, and left stirring overnight. All films processing was performed in an inert N_2 environment.

Optical characterization

For optical characterization, IS-19452 & IS-19507 samples in solution as well as on films were prepared and photophysical and Raman studies were performed to investigate structural differences amongst these two materials, and which impact these have on their electrical performance. The **Figure 3** shows the Raman spectra of both molecules measured on film as-spun.

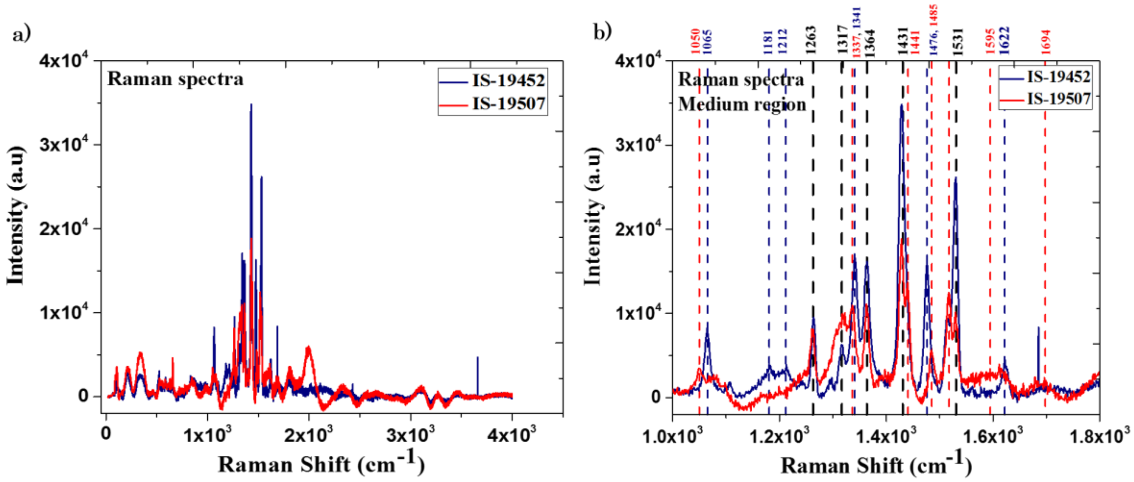

Figure 3: Raman spectra of **a)** IS19452 (blue), IS19507 (red) and **b)** Identification of Raman lines in the fingerprint region of IS-19452 (blue) and IS-19507 (red).

Femtosecond Raman spectroscopy (FSRS) was also performed on these two compounds for more detailed analysis and better understanding of structural differences amongst these two molecules. The collected data for this part remain under final analysis, as the outputs of FSRS are usually more difficult to interpret compared to the steady state Raman. The overall results from optical characterizations show minor differences in the absorption and PL spectra, while the Raman spectroscopy revealed noticeable differences in the Raman signature, due to the ortho-(IS-19507) and para-(IS-19452) substitution of benzene ring unit with fluorine molecules, which have an incidence on the transport properties of the materials.

Electrical characterization – Transport properties

For the electrical measurements, hole-only and electron-only devices with the following architectures were prepared: ITO/PEDOT:PSS/ IS-19452 or IS-19507 /MoO_3/Ag (hole-only) and ITO/PFN/ IS-19452 or IS-19507 /Ca/Al (electron-only). Current-voltage (JV) and Impedance spectroscopy were used to estimate the charge carrier mobility, as well as to study charge transport in these materials.

The JV characteristics of hole-only devices of IS-19452 and IS-19507 for films prepared in C = 20 $mg.ml^{-1}$ are shown below:

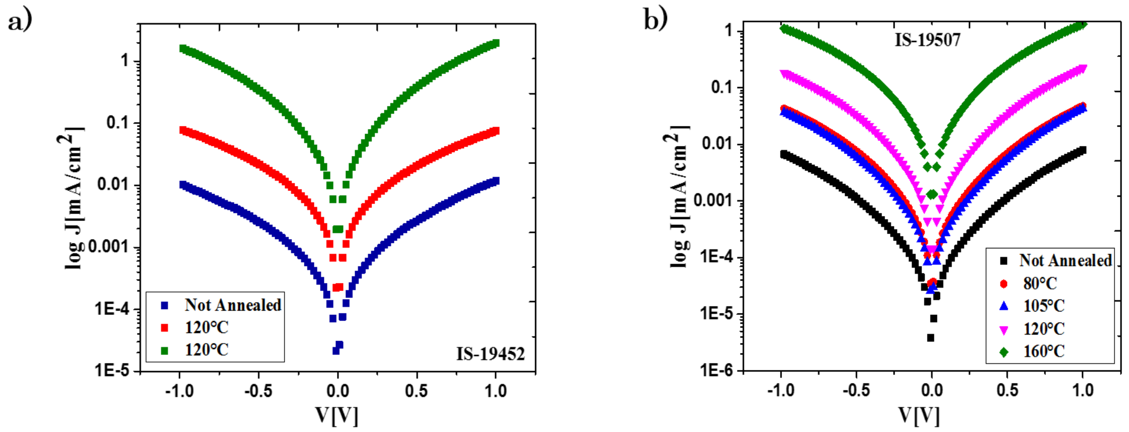

Figure 1 : Current density-voltage (JV) characteristics for diodes prepared with **a)** as-spun IS-19452 films (blue) and IS-19452 films annealed at 120 ^{o}C (red) and 160 ^{o}C (green) **b)** as-spun IS-19507 (black), and IS-19507 films annealed at 80 ^{o}C (red), 105 ^{o}C (blue), 120 ^{o}C (pink) and 160 ^{o}C (green).

The current density of annealed films for both materials is higher than in as-spun films, and current density increases with increasing annealing temperature.

We performed impedance spectroscopy in order to understand the electrical properties of these new materials in more detail and the carrier mobility was measured in both materials, as shown in the **Figure 2** below. For Is-19452, carrier mobility increases over two orders of magnitude from $\mu = (2.5 \pm 0.1) \times 10^{-7} cm^2\ V^{-1}\ s^{-1}$ in as spun films to $\mu = (4.3 \pm 02) \times 10^{-5}\ cm^2\ V^{-1}\ s^{-1}$ in films annealed at 160 ^{o}C. In parallel, carrier mobility in IS-19507, increases even more up to three orders of magnitude from $\mu = (1.7 \pm 0.1) \times 10^{-8} cm^2\ V^{-1}\ s^{-1}$ in as spun films to $\mu = ((1.0 \pm 0.06) \times 10^{-5}\ cm^2\ V^{-1}\ s^{-1}$ in films annealed at 160 ^{o}C. We observe no voltage dependence in the carrier mobility in both cases, demonstrating the high crystallinity of both materials.

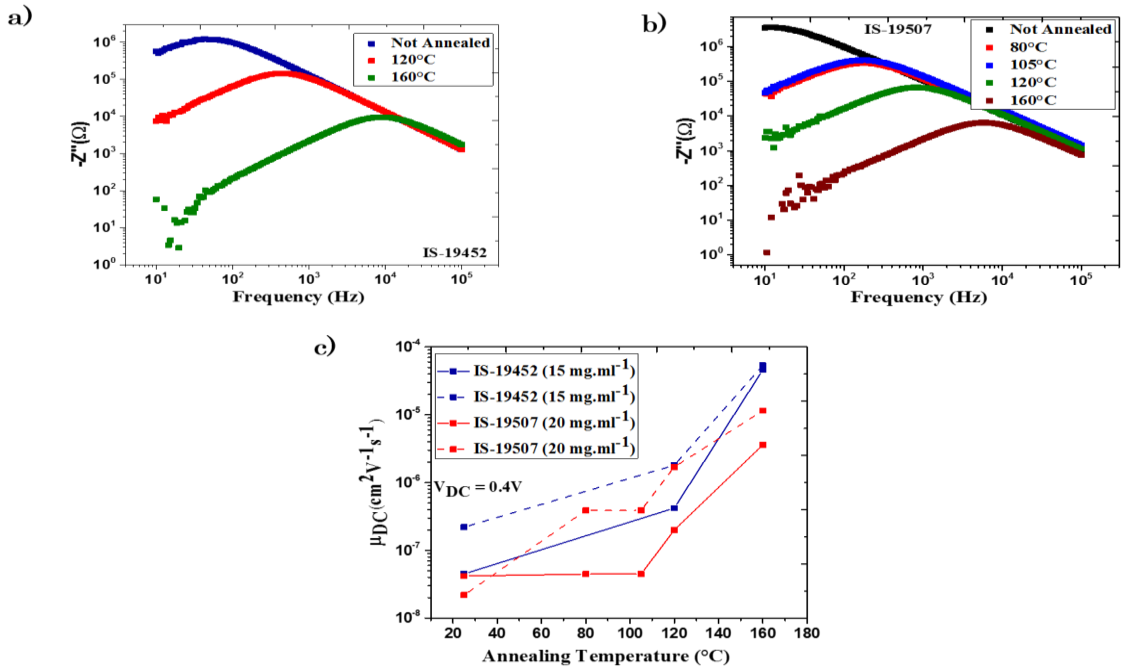

Figure 2. **a)** Bode plots for -Z" versus f spectra for the samples of **a)** IS-19452 with annealed films (120 ^{o}C – red, and 160 ^{o}C – green) and **b)** IS-19507 with annealed films (80 ^{o}C (red), 105 ^{o}C (blue), 120 ^{o}C (green) and 160 ^{o}C (wine)). **c)** The carrier mobility in IS-19452 and IS-19507 versus annealing temperature.

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Personal Experience

Beside intense electrical characterization my research stay allowed me to perform on the new materials, it also allowed me to learn the principles of optical spectroscopic techniques (Steady state Raman and FSRS). This research stay did not only give me the opportunity to acquire high quality experimental results for my PhD work, but also to acquire experience on new techniques which can be transferred between the groups in Oldenburg and Amsterdam. Also, experiencing a different working environment give me the opportunity to gain a rich scientific as well as an enjoyable human experience, which without a doubt, would be definitively helpful for my future career.

Conclusions

This research stay allowed to investigate successfully, the structure-functions relationship amongst two materials very similar in their chemical structures, but exhibiting difference in their Mesophase. A main finding was that relatively high carrier mobility was achieved in both materials after annealing in the different Mesophase. However, the IS-19452 show higher mobility in general in comparison with IS-19507 which show a smectic phase. This results suggest that the perfect crystalline order (smectic phase), does not necessarily guarantee better charge transport in LC dyes. Optical characterizations also displays structural differences amongst the two material. The overall results indicate that beyond that well known displays applications, LC dyes are promising materials for organic electronic in the future.

Outlook

The work is currently being carried out in the framework of a common PhD project, supervised both by Prof Juergen Parisi and Dr Elizabeth von Hauff. The goal of this particular research exchange was a common paper between the two groups, and a paper with the outcome results is now in preparation. The group of Elizabeth von Hauff at the VU has complementary sample preparation infrastructure to the EHF (Parisi) which facilitates future exchanges of group members for common measurements.

(1) Coropceanu, Veaceslav, et al. "Charge Transport in Organic Semiconductors." *Chemical reviews* 107.4 (2007): 926-952.

(2) Bässler, Heinz, and Anna Köhler. "Charge Transport in Organic Semiconductors." *Unimolecular and supramolecular electronics I*. Springer Berlin Heidelberg, 2011. 1-65.

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Federal Ministry of Education and Research