



Mass spectrometric analysis of impurities in crystalline organic semiconductors

A. Voloshenko^a, K.J. Tan^b, C. Kloc^{b,*}, O. Lev^{a,b,*}, M. Shelkov^a, S. Sladkevich^a, P.V. Prikhodchenko^a, J. Gun^a

^a Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

^b School of Material Science and Engineering, Nanyang Technological University, Singapore

ARTICLE INFO

Article history:

Received 20 June 2012

Received in revised form 25 October 2012

Accepted 1 November 2012

Available online 28 November 2012

Keywords:

GC–SMB–EI–MS

Supersonic molecular beam (SMB)

Crystalline organic semiconductors

Pentacene

Anthracene

Tetracene

ABSTRACT

Crystalline acenes are promising organic p-type semiconductors for future electronics. However, despite their importance to emerging and future electronics and in distinct contrast to the large technological care that is devoted to control the impurity levels in inorganic semiconductors, organic impurities in crystalline organic electronic components were left largely unexplored.

The impurities in commercially available crystalline anthracene, tetracene and pentacene were analyzed and compared to crystalline organics that were obtained by two methods: solution (flux) growth, where the solvent was naphthalene, solid at room temperature but liquid in the crystal growth temperature range and by physical vapor transport. The impurities were identified by different methodologies: GC–EI–MS, a gas chromatograph GC equipped with an electron ionization ion source and a single quadrupole mass analyzer; GC–SMB–EI–QQQ–MS, a GC equipped with a low temperature electron ionization ion source (supersonic molecular beam, SMB), and a triple quadrupole mass analyzer; high resolution MALDI–TOF–TOF–MS, matrix assisted laser desorption with two time of flight analyzers in series; and ESI–Q–TOF–MS, electrospray ionization mass spectrometers equipped with a quadrupole mass analyzer and time of flight analyzers. Regular GC–EI–MS exhibited poor impurity identification power. The other three techniques provided complementary pictures of the various impurities present in these semiconductors with a significant overlap between identified impurities by the three instrumental approaches. GC–SMB–EI–QQQ–MS was the most revealing instrumental technique especially when combined with ChromatoProbe™ thermal desorption injector since the latter helped minimize degradation of pentacene during sample preparation. In all three organic semiconductors (OSs), the analyses clearly revealed a significant cleansing of the impurities by the physical vapor transport technique. The naphthalene flux crystallization method introduced a significant amount of naphthalene and benzothiofuran impurities, the latter being a known naphthalene impurity.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Organic semiconducting (OS) molecules are an attractive alternative for inorganic semiconductors [1,2]. Crystal-

line acenes such as anthracene, tetracene, and pentacene are all p-type semiconductors. Due to their simple molecular and crystalline structure these molecules may be considered as model substances for study of materials for future electronics [3].

The relevant characterization techniques for inorganic semiconductors can be readily realized for their organic counterparts, and indeed the bulk properties of the polycyclic aromatic hydrocarbons, PAH semiconductors, includ-

* Corresponding authors at: Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel.

E-mail addresses: CKloc@ntu.edu.sg (C. Kloc), ovadia@vms.huji.ac.il (O. Lev).

ing their band gap, charge carrier density and mobility have been amply studied. However, unlike inorganic semiconductors for which sophisticated surface characterization techniques are readily available, the identification of impurities in organic semiconductors is largely ignored by the material science community [4]. There is currently no clear understanding, let alone standard procedures, for the identification of chemical impurities in OS, and therefore the way such impurities affect their electronic performance is left unexplored. In spite of the vast number of application oriented studies about organic semiconductor thin film preparations (e.g. Refs. [5–8]), very few of them address the chemical purity of the OS [9–11]. Moreover, material scientists are left with no guidance regarding the effect of the commonly used purification by recrystallization on the level of impurities in OS.

Mass spectrometries (MSs) and particularly high-resolution MS are perhaps the most powerful tools for identification and quantification of unknown chemical impurities. Different impurities call for different instrumentation, but a comparison of the response of different MS instruments to OS impurities has never been undertaken. Here we present, for the first time, a detailed comparative analysis of several commonly used crystalline OS, namely, anthracene, tetracene, and pentacene by different hyphenated MS techniques. Both commercially available polycrystalline semiconductors and home – synthesized, high – purity single crystals were studied by different analytical approaches.

The first analytical approach was to identify impurities in the bulk material by using a separation technique (GC) coupled to electron ionization (EI) ion source and quadrupole mass analyzer. A variant of this technique involved the use of supersonic molecular beam (SMB-EI) ion source which was recently commercialized by Aviv Analytical [12]. The technique is still based on electron ionization, but, unlike regular EI, ionization is carried out at very low temperature, thereby minimizing both vibrational energies and the degree of fragmentation. Thus, the method can be viewed as a compromise between hard ionization typical of conventional EI and soft ionization that is usually encountered in laser desorption and electrospray ionization. The SMB-EI provides sufficient fragmentation to allow identification by comparison to conventional EI libraries, but the molecular ion remains at high abundance, which provides improved identification power. Additionally, the SMB-EI is compatible with much larger flow rates, and thus it was possible to install a short capillary column which allows faster (15 min), high throughput analysis. High flow rate and shorter retention time in the GC column reduce the degree of in-column fragmentation and improve impurity identification. In this research we used both short (4 m) and long (30 m) capillary columns to evaluate the effect of these two variants on compounds identification. Additionally, one of the GC injectors was equipped with a ChromatoProbe™, a thermal desorption auxiliary that allows evaporation of the solid OS and its introduction with the carrier gas (He) into the separation capillary. We have therefore carried out also a comparison between impurity identification by the GC–SMB-EI–QQQ–MS with and without thermal desorption. Acenes are known to undergo faster degradation in organic solvent compared to

their crystalline phase [13] and thus thermal desorption or laser desorption analysis may reduce impurities that were not originally present in the OS but introduced by dissolution prior to analysis.

Two other identification methods that were used in this research include electrospray mass spectrometer (ESI–MS) and laser desorption ionization MS (LD–MS). Electrospray is a soft ionization technique that is frequently used for identification of polyaromatic and heteroaromatic impurities. ESI analysis required dissolution of the analytes in toluene – acetonitrile mixture, which dissolves all three aromatic compounds. These analyses were carried out without prior chromatographic separation.

Since all target compounds were crystalline polyaromatics, we could use laser desorption (LD) instead of matrix assisted laser desorption (MALDI) for ionization [14,15]. Since the same instrument is used for MALDI and LD ionization, we reserve here the term LD for the ionization technique but still use the term MALDI for the instrument.

LD provides soft ionization and could be used without additional matrix that may introduce its own interferences and contaminants. Usually the matrices for MALDI are aromatic compounds that could interfere with the determination of the type of impurities that were targeted in this research [16–18]. When we started the research we hoped that LD would provide higher sensitivity for surface impurities of the crystalline phase, whereas the electrospray will be more sensitive for impurities in the bulk, but we could not substantiate this hypothesis in the current research.

In order to elucidate the cleansing effect of two common procedures for obtaining pure OS we investigated pentacene crystalline semiconductors that were prepared by physical vapor transport and by crystallization from liquid naphthalene flux and compared the OS impurities in the purified crystals to the original compound. Additionally, we evaluated the purification power of physical vapor transport in inert gas flow purification for all three OS crystals.

2. Materials and methods

2.1. Materials

Crystalline anthracene, tetracene, and pentacene were purchased from Sigma–Aldrich and used as is. The synthesis and purification procedures used by the vendor are not disclosed. Two home – developed crystal growth–purification methods have been used. Crystalline OS were prepared by the physical vapor transport in the flow of inert gas and by solution growth from liquid naphthalene.

2.2. Physical vapor transport

Briefly, commercial anthracene, tetracene, and pentacene were sublimed in temperature gradients, in open systems where argon has been used as a transport agent [19,20]. Heavy molecules left in the source zone, solvents and other small molecules were removed with the gas flow

Download English Version:

<https://daneshyari.com/en/article/1263979>

Download Persian Version:

<https://daneshyari.com/article/1263979>

[Daneshyari.com](https://daneshyari.com)