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Towards reliable charge-mobility benchmark measurements for organic semiconductors

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ABSTRACT

Charge carrier mobility is a figure of merit commonly used to rate organic semiconducting materials for their suitability in applications such as solid-state lighting or photovoltaics. Although large variations are found in published mobility values on identical materials, there is little open discussion in the literature of the reproducibility of these results. We address this with an interlaboratory study of mobility measurements performed on a set of organic semiconductors using the space-charge limited current method. We found mobility measured on nominally identical devices could vary by more than one order of magnitude, with the largest sources of variation being poor electrodes and film thickness variation. Moreover, we found that mobility values extracted from identical data by different scientists would typically vary by a factor of 3. We propose a protocol for analysis and reporting that was found to reduce this analysis variation to as little as 20%. We also present general guidelines for improving the reproducibility of benchmark mobility measurements.

1. Introduction

Organic semiconductors are used in the emerging organic electronics industry as the essential active materials for functional devices such as organic thin-film transistors (OTFTs), organic photovoltaics (OPVs) and organic light-emitting diodes (OLEDs). As the industry evolves, there is an increasing demand for simple, reproducible measurements of the critical material parameters that affect device performance. These are typically used to optimise processes or to assess the potential of new materials in research and development programmes, or as quality control for material production.

Charge transport in organic semiconductors is critical to good device performance. In OPVs, efficient, balanced charge transport reduces current losses from recombination and series resistance losses under high irradiances [1–4]. In OLEDs, good charge transport is important for achieving a combination of high efficiency and high brightness [5]. Charge transport in organic semiconductors has been described by models of varying complexity, including device-level and molecular-level models requiring many parameters [6–10]. However, engineers focussed on applications often favour reduction to a simpler description with a single parameter that can be used to benchmark and compare different materials. Typically the preferred parameter is 'mobility' – the mean charge velocity divided by the electric field.

In disordered materials, such as typical organic semiconductors or amorphous inorganic materials, care needs

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to be taken with the concept of mobility. Scher and Montroll noted in 1975 that "*...the simple notion of a mobility, field dependent or otherwise, is very limited.*" [11] Orders of magnitude variations in mobility values measured on the same material using different techniques are common and widely accepted in the field; though they are not often candidly discussed, and even less often quantified. Nevertheless, mobility measurements can be useful for screening applications if properly used. In the context of a small interlaboratory study of mobility measurements on a set of organic semiconductors, this paper is intended to help readers to understand and manage some of the uncertainties in mobility measurements. The focus is on mobility measurements applicable to diode structures, such as OLED and OPV devices. The results do not apply to OFETs, which operate in a completely different transport regime [12,13] and have relatively harmonised measurement procedures. We briefly discuss the challenges and advantages of different techniques and focus on the simplest and most versatile method: the space-charge limited current–voltage (SCLC) technique. We identify the major sources of experimental errors that affect device reproducibility. Strikingly, we demonstrate that different approaches to data analysis are one of the major sources of uncertainty when extracting mobility data from these measurements. To tackle this issue and improve reproducibility of measurements, we propose a protocol for data analysis and show that standard deviation can be significantly reduced.

In Section 2 of this paper we describe the fabrication of devices used for experimental studies. In Section 3 we briefly compare different methods of measuring mobility in diode structures. In Section 4 we report on the reproducibility of the SCLC technique and propose a protocol for data analysis. In Section 5 we use sensitivity analysis to analyse the sources of variation in SCLC mobility measurements. In section 6 we discuss and summarise our conclusions. Readers who are familiar with the SCLC technique may wish to skip directly to Section 4, 5, or 6.

2. Device fabrication

Sandwich-type devices were fabricated by spin-coating organic semiconductor films of different thicknesses (from 60 nm to 1100 nm) from toluene solution onto patterned transparent indium tin oxide (ITO) coated glass substrates coated with poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) (Clevios AI4083). These were capped with thermally evaporated top electrodes, defining active device areas of 0.04 cm^2 overlap between the top electrode and ITO.

For the semiconductor layer, three fluorene-based alternating copolymers were studied: F8BT, TFB and PFB (see supplemental information for chemical structures [14]). Previous studies of similar materials have found hole transport to be relatively poor, and characterised by strong energetic disorder [6,15,16]. They present an interesting challenge for studying charge transport measurements, as mobility is predicted to vary with electric field, charge density and time (under transient conditions), and were chosen to present a "worst-case" scenario. These materials are anecdotally reported to be relatively air stable. The approximate highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies are displayed in Fig. 1. PEDOT:PSS acts as a transparent hole-injection layer (HIL) and electron-blocking layer with a work function of around 5.1–5.3 eV [17]. For some materials, an energetic barrier is expected for hole injection from PEDOT:PSS (i.e. 0.5–0.9 eV barrier for F8BT). Gold was used as a top electrode. The Fermi level of gold (work function ~4.5 eV under these conditions [18,19]) is expected to lie within the band gap of all three materials, presenting an energetic barrier to injection of both electrons and holes. A duplicate set of devices was created with a 5 nm interlayer of MoO_3 thermally deposited between the polymer semiconductor layer and the gold top electrode. MoO_3 acts as a HIL with a high work function (between 5.6 eV and 6.8 eV [20]) that is sufficient to inject holes efficiently into most conjugated polymers, including F8BT [16,21].

Devices were fabricated in nitrogen-filled glove boxes. For interlaboratory studies, duplicate sets of devices were fabricated at the same time and transported in vacuum-sealed packages. Devices were stored in nitrogen- or argon-filled gloveboxes and measured in air-tight containers filled with gas from the gloveboxes. During transport and measurement of the devices, monitoring of the quality of the atmosphere was impossible. These conditions are typical of those used for research and development in the field.

3. Mobility measurement techniques

In our initial study, mobility measurements were performed at different laboratories using a range of techniques. These were the steady-state space-charge limited current (SCLC) method and the transient methods: time-of-flight (ToF), dark-injection transient current (DITC) and charge extraction by linearly increasing voltage (CELIV). SCLC was the only technique that was able to extract a mobility measurement on every device. However, as we describe below, this does not necessarily mean that the extracted mobility values were consistent. The transient

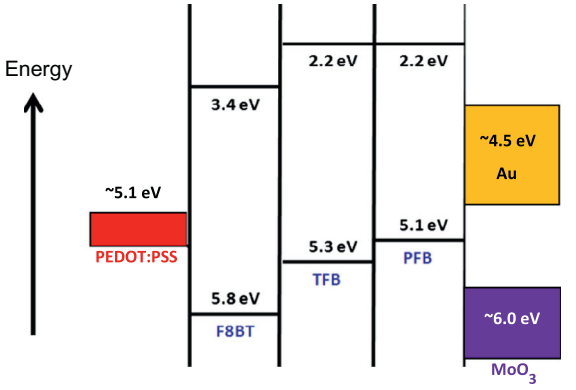

Fig. 1. Approximate energy-level alignment diagram showing the LUMO and HOMO energies of the three organic semiconductors studied and the Fermi levels of three electrode materials. Note that typical uncertainties on these values are ±0.2 eV.