



# Influence of molecular architecture and processing on properties of semiconducting arylacetylene: Insulating poly(vinylidene fluoride) blends

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## ABSTRACT

Blends of chemically readily accessible, small-molecular arylacetylene derivatives with poly(vinylidene fluoride) (PVDF) are presented that allow reliable solution processing of field-effect transistor (FET) architectures with electronic characteristics comparable to those of the neat semiconductors. We demonstrate that having the chemical means and corresponding processing protocols to control solid-state microstructures by either adjusting the chemical nature of the organic semiconductor, blend composition or deposition temperature, permit straight-forward comparison between materials and allow probing if electronic characteristics are affected by the chemical structure of the organic semiconductor and/or selected processing protocols.

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## 1. Introduction

Over the past three decades, the field of organic electronics has advanced rapidly, driven by the synthesis of new semiconducting small molecules, oligomers and polymers that enabled better devices, and new functionalities. The strong interest in organics stems from the fact that this class of semiconductors holds the promise of cost-efficient processing characteristics, light weight, (semi-) transparency and mechanical flexibility. Most importantly, they have the potential to be readily chemically tailored to fine tune properties such as charge transport, light absorption, emission, etc., to address various application needs [1–13].

Major challenges, however, still exist. Main drawbacks of many of the commonly used materials are, for instance,

their often modest electrical performance, which in general remains well below that of the widely deployed inorganic materials (e.g. amorphous hydrogenated silicon), and their vulnerability to ambient oxidants, as many of the materials tend to degrade upon contact with air and/or light [14–17]. This environmental sensitivity of organic semiconducting compounds requires vacuum- or inert atmosphere-based device fabrication steps [18–21] and encapsulation in barrier (sandwich) structures [22,23]. Unfortunately, such stringent processing protocols significantly contribute to the cost of organic-based electronics, which has not declined as quickly as originally envisioned, while competitive technologies have enjoyed more rapid than anticipated economic advantage [24]. All these constraints render organic-based devices less obvious as a viable alternative to more conventional electronics.

This development may, however, be halted – if not reversed – provided that new organic semiconductor systems are developed that exhibit high charge-carrier mobilities, environmental stability and a beneficial econ-

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omy of scale both through straight-forward synthesis and processing. While a limited number of high mobility, environmental stable materials have been advanced [7,25–30], one of the key challenges, which remains and limits further progress, is the provision of straight-forward and meaningful comparisons between the electronic properties of different compounds. Such comparisons would allow for efficient materials design and screening but necessitates high reproducibility in synthesis, processing and reliable device fabrication and characterization.

Blending of organic semiconductors with insulating (semi-crystalline) polymers has been shown to be a useful strategy to address, among other things, the latter two issues [31–38]. In addition, blending with properly selected commodity polymers to the semiconducting material(s) should enable control over melt- and solution viscosity. In the case of small-molecular semiconductors, a suitable polymer matrix may furthermore be mandatory to meet the ink rheology requirements for specific printing steps in solution-processed devices. From a device point of view, blending is an interesting approach, as it may also lead to multi-component structures with a property matrix that is often not accessible with the individual components. The latter is possibly best exemplified by organic semiconductor:insulator blends, which – under appropriate processing conditions – feature excellent performance in organic field-effect transistors (OFETs) and organic photovoltaics (OPVs) at remarkably low semiconductor contents combined with highly desirable mechanical properties when a tough insulating component is utilized [31]. Besides improved and reliable film formation, blending promises the prospect for major cost reduction, truly “flexible” electronics and, often, significantly enhanced environmental stability of devices produced with them.

In the present study we explored bi-component blends comprising arylacetylenes and the insulating poly(vinylidene fluoride) (PVDF). PVDF was selected as the insulating component as this polymer has been shown to allow film processing at room temperature of, for instance, poly(3-hexylthiophene) (P3HT):PVDF binaries [33]; this in contrast to, e.g., blends based on high-density polyethylene which require deposition temperatures above  $\sim 70^\circ\text{C}$  [31,32]. For the semiconducting species, we focused on *small-molecular* arylacetylenes [39–50]. From a synthetic point of view these compounds exhibit a number of advantages, including availability of efficient synthetic protocols [51–59] that offer the possibility to access in large quantities a broad variety of molecules with specific geometries and flexibility in new conceptions of steric and conformational structures. In addition, their shape-persistent rod-like structures may be of beneficial use for the construction of a broad spectrum of nano and microstructures. A further major advantage of arylacetylenes is that they can be readily synthesized from easily accessible precursors, do not require exotic, rare materials, reducing risks regarding materials supply or costs; their production can easily be scaled up; and, finally, the compounds can readily be isolated in high purity.

Here, we concentrate on arylacetylenes with an anthracene [60,61] backbone, since this core may enable enhanced solubility and stability when compared to, for

instance, pentacene, which has become a benchmark in the organic electronics field. Moreover, the anthracene core is a beneficial chromophore unit. Importantly, their chemical structure allows for derivatization with flexible chains at the terminal phenyl-ring systems to modulate the phase behavior and solubility of the resulting arylacetylenes. Those latter attributes permit to manipulate their solid-state structure over a large range of length scales, the influence of which on simple electronic characteristics being the subject of this study.

## 2. Experimental

### 2.1. Materials

9,10-Bis(phenylethynyl)anthracene (**1**) was purchased from Alfa Aesar GmbH & Co KG, Karlsruhe, Germany, and used as received. 9,10-Bis[3,4-bis(hexyloxy)phenylethynyl]anthracene (**2**) was synthesized according to a previously reported procedure [44]. Poly(vinylidene fluoride) (PVDF) ( $M_w = 534 \text{ kg/mol}$ ) was acquired from Aldrich, Steinheim, Germany. Cyclohexanone was purchased from Acros, Geel, Belgium, and used as received.

### 2.2. Sample preparation

Blends for thermal analysis and optical microscopy were prepared by co-dissolving the semiconducting species and PVDF in cyclohexanone ( $\sim 2 \text{ wt.}\%$  total solids content) at  $100^\circ\text{C}$ , followed by solvent evaporation at ambient conditions or at  $\sim 100^\circ\text{C}$ . Blends for OFETs were prepared by co-dissolving the different materials in cyclohexanone ( $\sim 6 \text{ wt.}\%$  solids content) at  $100^\circ\text{C}$ , followed by subsequent adjustment of the solution temperatures to the respective processing temperatures of  $25, 50, 75$  or  $100^\circ\text{C}$ . To allow film fabrication under isothermal conditions, solutions, metal substrate holders and substrates (doped silicon–silicon oxide ( $\text{Si-SiO}_2$ )) were equilibrated for ca. 10 min at the designated temperature before spin-drop-casting active layers with a Laurell WS-400B-6NPP/LITE spin-coater at 500 rpm. Note, however, that dissolution temperatures below  $100^\circ\text{C}$  could have been applied, if required, as indicated by the crystallization temperature/composition diagrams of the blend components (*cf.* Figs. 1 and 2b). In addition, the substituted derivative **2** allows fabrication of solutions that are stable under ambient conditions and, hence, can be stored at room temperature without featuring precipitation of the solutes.

### 2.3. Characterization

Differential scanning calorimetry (DSC) was conducted under  $\text{N}_2$  atmosphere at a scan rate of  $10^\circ\text{C}/\text{min}$  with a Mettler Toledo DSC 822<sup>e</sup> instrument. For DSC analysis of **1**, **2** and PVDF in cyclohexanone, medium pressure  $120 \mu\text{l}$  Mettler stainless steel crucibles sealed with Viton O-rings were utilized. The total sample weight varied between 20 and 40 mg. For characterization of the dried blend films, amounts of  $\sim 5 \text{ mg}$  were sealed in Al standard  $40 \mu\text{l}$  crucibles.

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