DATA-ENABLED EXPERIMENTAL DEVELOPMENT OF POLYMER-BASED ORGANIC ELECTRONICS

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Abstract

Data science approaches have yielded pathways toward "big data analytics" for the accelerated development of many material systems. However, tremendous challenges exist in applying widespread, data-driven approaches to facilitate the accelerated development of electronic devices formulated from polymer semiconductors. Such polymer materials have demonstrated unprecedented performance for flexible, stretchable, and deformable device applications, though their discovery remains largely trial-and-error. A foremost challenge is the availability of experimental data that can yield the requisite knowledge necessary to inform robust performance and formulation precision at the manufacturing scale. The reliability of available experimental data to this end, such as in literature, is hindered by the need to interrogate the relevant process parameters and structural features in both solution and in thin film. This presentation details progress on the implementation of informatics methodologies for the development of polymer-based organic semiconductor technologies. The integration of high throughput experimentation laboratory techniques offers an avenue to traverse the small data gap afforded by the organic semiconductor parameter space. Robust data management systems provide a foundation for schema design and solutions for the challenges in small, sparse, materials data. Finally, the incorporation of "small data analytics" approaches on literature datasets provides a foundation for informing sequential experiments from which π-conjugated polymer domain knowledge can be extracted.

Keywords

Data science, Polymer semiconductors, Experimental design

Introduction

Development of π-conjugated polymers holds promise for modern applications in large-area, printed electronics due in part to their ease of solution processing. For example, these semiconducting materials are attractive as the active component in organic photovoltaic (OPV), organic light-emitting diode (OLED), and organic field-effect transistor (OFET) designs (Root et al., 2017).

A grand challenge within this materials domain is the immense parameter space offered by organic electronics. This design space is crowded by a variety of solution

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processing parameters in addition to the desired heterogeneous structure-property characterization data in the form of images, spectra, device measurements curves. In tandem with the traditionally "Edisonian" nature of experimental research within the organic electronics domain, the challenging design space creates a "small data" materials problem within which process optimization for high-performance devices becomes daunting (McBride et al., 2020).

Charge carrier mobility (μ), attained *via* the OFET device architecture, is the figure of merit in measuring the performance of organic electronics. As this performance metric is highly dependent on thin-film morphology, research efforts have focused on controlling this morphology by understanding and tuning polymer structure in solution (Xu et al., 2022). Therefore, the design space includes a large set of polymer characteristics (*e.g.*, monomer chemistry, molecular weight, polydispersity, charge carrier type, etc.), solvent properties, and parameters that relate to their complex polymer-solvent interactions. Furthermore, as semiconductor ink formulation frequently requires the blending of additional polymers, solvents, or small molecule additives, this design space quickly becomes unwieldy with the additional requirement to consider multicomponent compositional space.

Due to the challenges within this domain, the development of specialized approaches for analysis, data curation/storage, and experimentation is required to render the data-enabled development of π-conjugated polymer-based semiconductors more tenable (Callaway et al., 2022). This work will present a summary of work toward applying such techniques toward developing and understanding the behavior of next-generation polymer-based electronics.

High-Throughput Experimentation

In recent years, the materials community has invested resources in developing custom experimental methods to accelerate the experimental sampling of laboratory data. Such high-throughput experimentation (HTE) methods offer the potential to "bridge the small data gap" in polymer-based electronics. Gradient film methodologies are one common avenue for generating sample libraries on which multiple data points can be automatically measured via high-throughput characterization. For polymer thin-film applications, such as organic electronics, gradient sampling techniques leverage a solution-based mixing approach to deposit a continuous film sample with that spatially varies a desired parameter (*i.e.*, composition or blend ratio, thickness, etc.).

However, solubility is a major challenge in enabling HTE for many π-conjugated polymers because elevated temperatures create processing challenges in the small-volume mixing setups typically used for high throughput sample preparation. Providing high throughput experimentation beyond polymers only processible at ambient conditions, therefore, requires custom mixing protocols that consider solvent resistance, high viscosities, and temperature control to access a broader range of polymers that can be studied. For example, many semiconducting polymers of interest are studied in aggressive and/or chlorinated solvents and elevated temperatures to enable solution processibility.

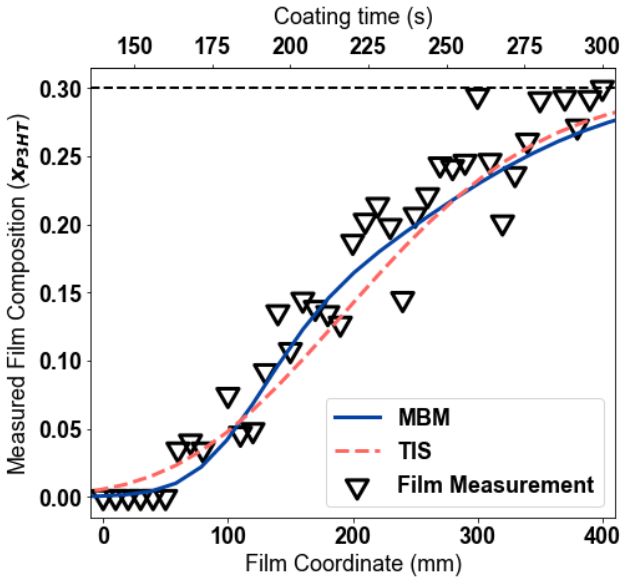

Figure 1. Film composition measurements (via x-ray photoelectron spectroscopy) of a P3HT:PS gradient thin film coated from a chloroform solution. MBM and TIS represent two residence time distribution models used to predict process conditions for the gradient film.

Recently, we have demonstrated a new gradient mixing and film deposition protocol that is capable of operating polymer solutions at elevated temperatures (Liu et al., 2022). Composition gradient poly(3-hexylthiophene)/poly(styrene) (P3HT/PS) films were demonstrated as a model π-conjugated polymer blend system (Figure 1), and poly(propylene)/poly(styrene) (PP/PS) films were used to demonstrate controllable composition gradients at temperatures of 110 °C. In particular, the latter system represents materials components in which gradient films are especially difficult to generate *via* existing coating approaches due to solubility constraints and viscosities at ambient conditions. The methodology developed and demonstrated here widens the range of solution processed materials that can be explored via high-throughput laboratory sampling and provides an avenue for efficiently screening multiparameter materials spaces even in polymer-based semiconductors thus far incompletely explored due to solubility constraints. Enabling this HTE protocol therefore opens avenues for populating the large datasets required to enable data-driven materials science in polymer semiconductors of interest.

OFET Database Design

Given the complexity of the design space and the wealth of information provided by prior experimental data, a robust experimental data management workflow is

required for enhancing research activities within polymer-based electronics. However, providing a repository to unify experimental data from literature and the laboratory within even a single polymer chemistry provides tremendous challenges due to small sampling size and inconsistency of reporting across data sources.

Structure-property data is heterogeneous, taking the form of spectroscopic signals, images, and device performance curves. From each of these pieces of information is frequently extracted a series of parameters either informed by established models or other custom methods (in the case of images). As structural ordering has long been established as an influential factor in controlling device performance, these extracted parameters serve to curate such structural information to elucidate the process-structure-property relationship.

"Non-relational" (NoSQL) database management systems (which exist alongside their relational (SQL) counterparts) have been deployed for a variety of use cases for computational data. Additionally, conceptual data modeling provides an opportunity to elucidate the organization of data and facilitates data unification under a common schema. In tandem, modern database management systems and conceptual modeling can facilitate the organized storage, workflow, and subsequent analysis of any data. Though many prime examples have been demonstrated for computational materials data, best practices for experimental materials data management as is not always clear due to the inconsistency challenges mentioned above.

Within our research workflow, we have applied the above tools to enable a searchable repository of OFET device data based on P3HT and poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl) thieno-3,2-b]-thiophene)] (DPP-DTT). Conceptual modeling facilitates the organization of curated experimental device information, including process, structure, and property features. Concurrently, NoSQL data management tools (using MongoDB) provide techniques to work around challenges related to inconsistent data reporting and missing data. Addressing these challenges using the techniques above will be discussed.

Knowledge Extraction from Small Materials Data

In addition to the storage of small materials data, we show that analysis of this materials data requires custom techniques to extract meaningful domain insights for polymer-based electronics. While small datasets may not always provide enough meaningful information to effectively feed machine learning models, data-driven tools can still be applied to extract domain knowledge and physicochemical motifs. Additionally, they can suggest work toward building a richer experimental dataset with the goal of enabling the application of more rigorous machine learning techniques.

For example, we have demonstrated a reduced design region (RDR) approach for learning from small datasets (McBride et al., 2018). This approach applies a custom classification algorithm to identify a design region within the available parameter space for which high performance experimental samples take place. The performance threshold for "high" and "low" performance is set by the user based on domain expertise. Two custom metrics are evaluated across all features to determine a small set of experimental parameters that are influential in describing high performance.

Our work therefore provides an avenue for selecting influential parameters and ranges to explore future experimental samples. In recent work, our RDR algorithm has enabled the small-data knowledge extraction or even machine learning predictions for PP-talc polymer composites (McBride et al., 2018), PET small molecule stabilizers (Liu et al., 2020) in addition to P3HT or DPP-DTT-based polymer electronics (Venkatesh et al., 2021).

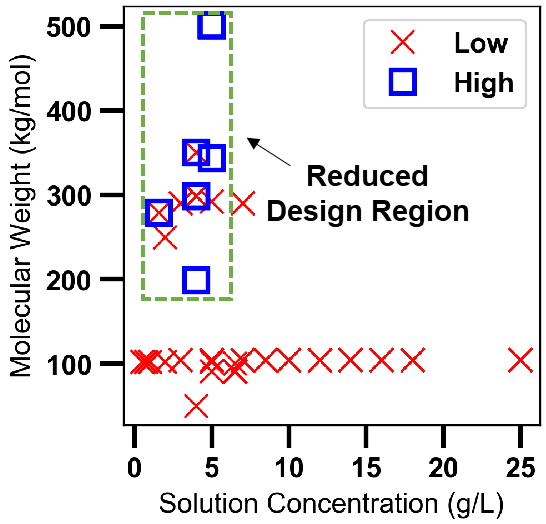

Figure 2. Two-dimensional reduced design region demonstration for DPP-DTT devices with hole mobility values above (squares) and below (X marks) a critical cutoff of 1 cm²/V•s. Dashed box suggests an experimental design region for future sampling.

Case Study: Identifying a Critical Overlap Concentration as an Influential Design Parameter in Organic Electronics

For the case of polymer electronics, we have shown that small data approaches applied to sparse literature data can enable a deeper study into process-structure-property motifs, therefore enhancing the experimental workflow. Our recent study applied the RDR technique to a literature dataset of n = 115 samples from 15 publications reporting the device performance of DPP-DTT across 34 different experimental parameters (Venkatesh et al., 2021). The data-driven algorithm identified molecular weight and solution concentration as influential parameters that provided the greatest reduction in the original experimental design space.

Interestingly, while high performance at higher molecular weights was not necessarily surprising, the results suggested an optimal window for concentration

might occur above a molecular weight threshold. This suggested that some critical process-structure motif occurs within this processing range (~2-8 g/L), despite the larger design region of concentration (1-25 g/L) in the curated literature.

To verify the performance sensitivity within this processing window, a high molecular weight (M_w = 290 kg/mol) sample of commercially available DPP-DTT was used to prepare and characterize a series of OFET devices coated from various solution concentrations using chlorobenzene as the solvent. Results showed a significant performance optimum within this concentration window, which verified the existence of high performance within the suggested design region informed by the algorithm.

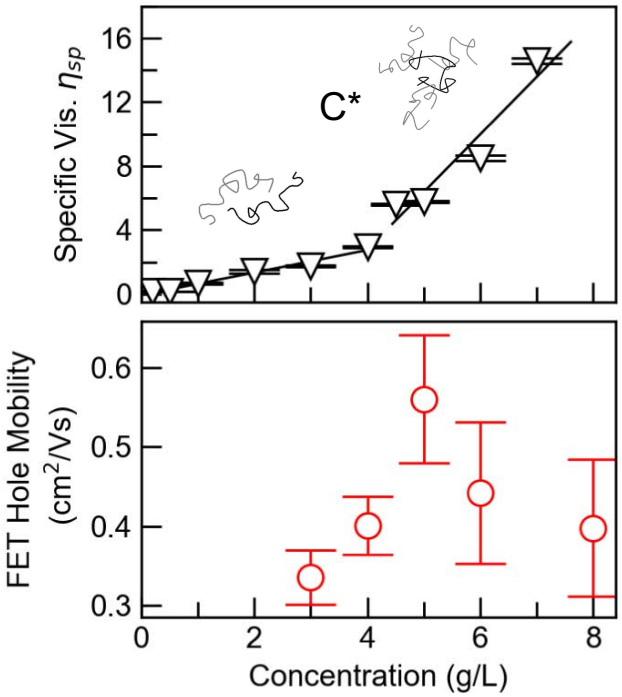

Figure 3. Device performance coincides with critical overlap concentration (C) in DPP-DTT. (a) Viscosity measurements of DPP-DTT dissolved in chlorobenzene solutions at 56 °C. (b) OFET hole mobility as a function of solution concentration*

The process-structure-property motifs responsible for this inflection in device behavior were further interrogated by subsequent spectroscopic, morphological, and solution-state studies. Results showed that the peak in hole mobility coincided with a critical overlap concentration (C*) behavior as measured by solution viscosity measurements. Accompanying studies facilitated by photophysical and spectroscopic measurements revealed insights about aggregate behavior in solution, suggesting a tunability of polymer chain backbone at varying concentrations. Further studies (*i.e.*, confirming behavior at various molecular weights, etc.) will also be presented.

Conclusions

The π-conjugated polymers that are studied as the active thin-film component in organic electronics are key candidates for future applications in clean energy, deformable devices, next-generation sensors, and more. However, moving beyond traditional one-factor-at-a-time approaches to experimentation will require the application of custom techniques that are tailored to the unique data types and information collected within this materials domain. Here, we detail a progress report toward enabling data-driven experimentation for π-conjugated polymers. Future work will focus on developing the feedback loops among the respective areas of data management, data collection, and data analytics to contribute toward accelerating experimental development within polymer-based electronics.

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