Tuning the hole mobilities in ordered small-molecule semiconductors by side-chain engineering and fluorine substitution

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Organic electronic devices such as organic solar cells, organic photodetectors, organic field-effect transistors, etc. have attracted significant attention over the last several decades due to their low-cost and unique characteristics e.g. lightweight, flexibility, and transparency [1]. The performance of organic electronics devices is mainly affected by charge transport characteristics of organic semiconductor materials used. Charge carriers transport in organic semiconductors can be improved by enhancing their crystallinity and self-ordering ability in solid state [2]. However, the majority of crystalline organic materials demonstrate poor solubility in organic solvents that hamper the fabrication of devices using high-throughput printing technologies. In this regard, the development of soluble small molecules with crystalline or liquid-crystalline ordering is considered an effective approach to obtain materials combining advanced optoelectronic properties, good solubility and improved charge transport characteristics.

In this work, we report the synthesis of four novel low molecular compounds based on alternate thiophene and benzothiadiazole blocks exhibiting crystalline or liquid-crystalline properties. It has been found that variation of side chains position in terminal thiophene rings and fluorine loading into benzothiadiazole moieties allow to tune optoelectronic properties of compounds as well as the microstructure of thin films. According to GIWAXS data, thermal treatment of certain samples led to reorganization of morphology that resulted in significant increase in hole mobilities of these materials. Annealing of fluorine-containing oligomer M4 induced the formation of domain structure of films, which hole mobilities were one order of magnitude higher as compared to untreated films. These findings provide a valuable insight into the structure-property relationships for designed small molecules featuring them as promising semiconductor materials for further developing high-performance organic electronics.

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