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Synthesis and optical and electrochemical properties of a bispyrimidinium-dibenzothiophene-*S*,*S*-dioxide-based cationic conjugated polymer

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ABSTRACT

A novel n-type cationic conjugated polymer (**PFSOmiCl**), consisting of bispyrimidinium-dibenzothiophene-*S*,*S*-dioxide and fluorene scaffolds, was developed from its polymeric precursor (**PFSOmi**) through an intramolecular cyclization reaction. In comparison with **PFSOmi**, **PFSOmiCl** exhibits significant bathochromical absorption and photoluminescence spectra in both solution and film form, as well as a more hydrophilic film surface. Cyclic voltammetry tests demonstrate that **PFSOmiCl** possesses a deep lowest unoccupied molecular orbital (LUMO) energy level of −4.18 eV, which is comparable to the LUMO energy levels of common fullerene derivatives. These unique properties endow **PFSOmiCl** with great utilization potential in organic optoelectronic devices. Moreover, this research offers a novel guideline for designing new conjugated polyelectrolytes.

1. Introduction

Conjugated polymers have been widely used in organic electronic devices, such as organic light-emitting diodes (OLEDs),[1–3] organic photovoltaics (OPVs),[4–6] organic field-effect transistors[7–9] and bio/chemosensors,[10,11] as a result of their significant advantages, including light weight, low cost, flexibility and large-scale solution processing. In comparison with the rapid development of p-type (hole-transporting) conjugated polymers,[12–14] the lack of high-performance n-type (electron-transporting) polymeric semiconductors has significantly hindered the improvement in performance of organic photoelectric devices. For instance, as only a small amount of n-type conjugated polymers and small molecules can adequately serve as electron acceptors in OPVs,[15–17] researchers have been forced to use high-cost fullerene derivatives as acceptors in order to improve efficiencies.[18] Alternatively, in the bio/chemosensor field, investigations have been mainly focused on synthesizing electron-donating polymers to detect electron-deficient analytes.[19–22] However, reports of electron-withdrawing polymers for the detection of electron-rich analytes are not in abundance.[23–25]

In past decades, water/alcohol-soluble conjugated polymers (WSCPs) have attracted significant attention and been extensively utilized in OLEDs,[26,27] OPVs[28,29] and bio/chemosensors.[30] By incorporating surfactant-like polar groups (e.g., ammonium,[31,32] sulfonate and[33] phosphonate groups[34]), conjugated polymers can be dissolved in highly polar solvents, such as water, dimethyl sulfoxide (DMSO), methanol and so on. This kind of unusual solubility offers an opportunity to fabricate multilayer optoelectronic devices via orthogonal solvent processing techniques without interfacial erosion problems, when WSCPs are used as electrode interfacial layers in OLEDs and OPVs.[27,28] In addition, solubility in aqueous media, which is an essential property for biosensors, makes WSCPs capable of interacting with biomacromolecules that are only soluble in aqueous solution.[30] However, most of the reported WSCPs are based on electron-rich backbones, and ideally, n-type WSCPs with electron-deficient backbones are more efficient for electron transportation and extraction in organic electronic devices.[35] Hence, it is necessary to develop new n-type WSCPs to improve the performance of OPVs, OLEDs and perovskite solar cells (PVSCs), as well as to detect electron-donating analytes.

Recently, the Swager group synthesized a series of cationic conjugated polymers composed of bispyridinium-phenylene

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scaffolds that showed high electron affinities and conductivities.[24,25,36–38] Because of their significant electron-withdrawing abilities, some of these WSCPs exhibited admirable sensing performance when they were used to detect electron-donating analytes (e.g., volatile amines and caffeine).[24,25] Su and co-workers prepared three n-type conjugated small molecules containing bispyridinium–phenylene units, and used one of them for improving the cathode interfacial contact of an OPV.[39] Interestingly, they found that their material could create an interfacial dipole between the active layer and metal cathode, which was consistent with the research of Kim and co-workers.[40] This dipole could reduce the work function of cathode and thus increase the built-in potential across the device. As a result, the short-circuit current (J_{sc}), open-circuit voltage (V_{oc}) and fill factor (*FF*) of the OPV were simultaneously enhanced. Based on the above results, cationic conjugated polymers and small molecules containing bispyridinium units may be a class of high-performance materials for organic photoelectric devices and sensors.

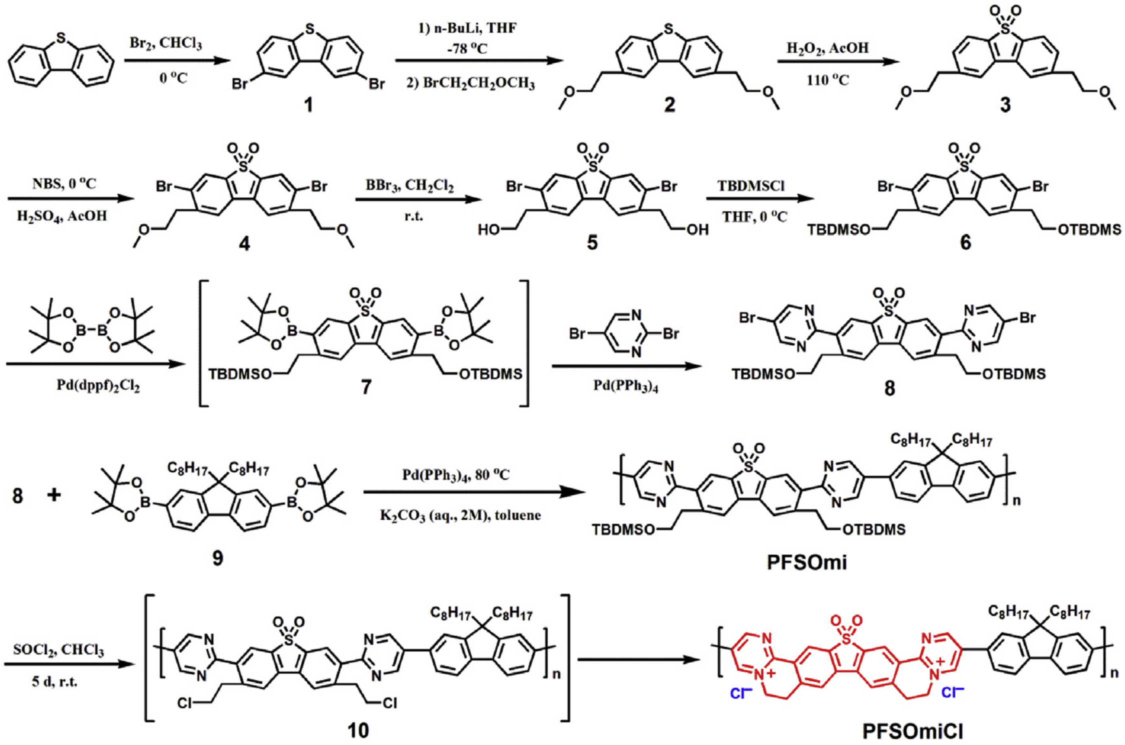
Dibenzothiophene-*S*,*S*-dioxide (FSO) is a well-known n-type aromatic heterocycle that exhibits good thermal stability, high fluorescence efficiency, high electron affinity and electron-transporting ability.[41–44] Previously, we synthesized a family of blue, green and red light-emitting polyfluorenes (PFs) containing FSO units.[1] These polymers exhibited excellent electroluminescent performance with maximal efficiencies of 7.0, 17.6 and 6.1 cd A^{-1} for the blue, green and red light-emitting polymers, respectively. Subsequently, we introduced FSO moieties into the backbones of alcohol-soluble PFs containing amino groups.[45] When these polymers were utilized as cathode interlayers in OLEDs and OPVs, some of them displayed better modification performance than the famous interfacial material, poly[(9,9-bis(3-(*N*,*N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)], which was attributed to enhancements in the electron-transporting properties of these polymers by the FSO units. In addition, we also obtained a series of novel polycyclic aromatic compounds based on FSO-fused seven rings, which displayed high thermal stabilities and photoluminescence quantum yields.[46]

Previously, we demonstrated the successful synthesis of two novel cationic conjugated small molecules based on bispyridinium-FSO or bispyrimidinium-FSO segments, and their photoelectronic properties were investigated in detail.[47] Herein, we report the design and synthesis of a novel n-type cationic conjugated polymer (**PFSOmiCl**), consisting of bispyrimidinium-FSO and fluorene scaffolds. The bispyrimidinium-FSO unit endows the polyelectrolyte with high electrophilicity and a planar structure for π-electron delocalization. In addition, the pyrimidinium rings offer this polymer versatile solubility and processability in highly polar solvents. The octyl group side chains within a fluorene repeating unit grant the polymer good film-forming ability. Therefore, this type of WSCP may be a potential material for organic electronic devices, such as OLEDs, OPVs, PVSCs and bio/chemosensors.

2. Results and discussion

2.1. Synthesis

The synthetic route of **PFSOmiCl** is shown in Scheme 1. Compound **1** was reacted with n-BuLi in anhydrous tetrahydrofuran (THF) at −78 °C, after which the reaction was quenched by 1-bromo-2-methoxyethane. Compound **3** was obtained as a white solid by oxidizing **2** with a H_2O_2 aqueous solution. Subsequently, bromination of **3** with *N*-bromobutanimide in the mixed solvent of concentrated H_2SO_4 and AcOH (3:1, *v*/*v*) offered compound **4**. It was found that the presence of concentrated H_2SO_4 was indispensable for improving the reaction yield. Compound **4** could be separated from the byproducts by column chromatography on silica gel with ethyl/petroleum (1/1, *v*/*v*) as the eluent. Then, elimination of the methyl groups within the side chains of **4** by BBr_3 generated **5.** Compound **5** has poor solubility in common organic solvents (THF, $CHCl_3$, toluene and so on). Compound **6** was obtained through the



Scheme 1. Synthetic routes for the monomers and polymers.