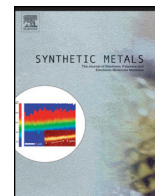




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## Investigation of the effect of conjugated oligoelectrolyte as a cathode buffer layer on the photovoltaic properties

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## ABSTRACT

A series of conjugated oligoelectrolytes consisting of fluorene and phenothiazine, 6,6',6'',6''',6''''-((10-hexyl-10H-phenothiazine-3,7-diyl)bis(9H-fluorene-9,9,2-triyl))tetrakis(N,N,N-trimethylhexan-1-aminium) bromide (FFiF), 6,6',6'',6''',6''''-((10-(4-(trimethylammonio)butyl)-10H-phenothiazine-3,7-diyl)bis(9H-fluorene-9,9,2-triyl))tetrakis(N,N,N-trimethylhexan-1-aminium) bromide (FPiF) and 6,6',6'',6''',6''''-((10-hexyl-10H-phenothiazine-3,7-diyl)bis(9H-fluorene-9,9,2-triyl))tetrakis(N,N,N-trimethylhexan-1-aminium) bromide (FPF), are utilized as the cathode interfacial layer in conventional-type polymer solar cells based on P3HT and PCBM. Insertion of these interfacial layers between P3HT/PCBM active layer and the metal cathode increases overall power conversion efficiency from 2.76% (reference device) to 2.81%, 3.04%, and 3.37% of devices with FPiF, FFiF, or PPF-coated Al, respectively, primarily due to the reduction of the metal work function through the introduction of conjugated oligoelectrolytes (COEs). This result comes from the difference moiety (i.e., phenothiazine or fluorene) and arrangement of sides chains with quaternary ammonium bromide (QAB) on trimer backbones. The conformation of FFiF is expected to be not exactly in a zigzag arrangement, while the zigzag conformation is expected for the alternated oligomer based on phenothiazine and fluorene (FPiF and PPF). Therefore, the number of accumulated QAB in the side chains of FPiF at the surface of cathode will be smaller than that of FFiF or PPF. The larger amount QAB groups gathering near the cathode layer leads to the bigger in reduction of metal work function. Additionally, PPF coated Al shows the lower work function than that of FFiF coated Al, even though FFiF contains more QAB groups accruing at cathode layer. Thus the device with PPF modified-Al displays the best performances among the devices.

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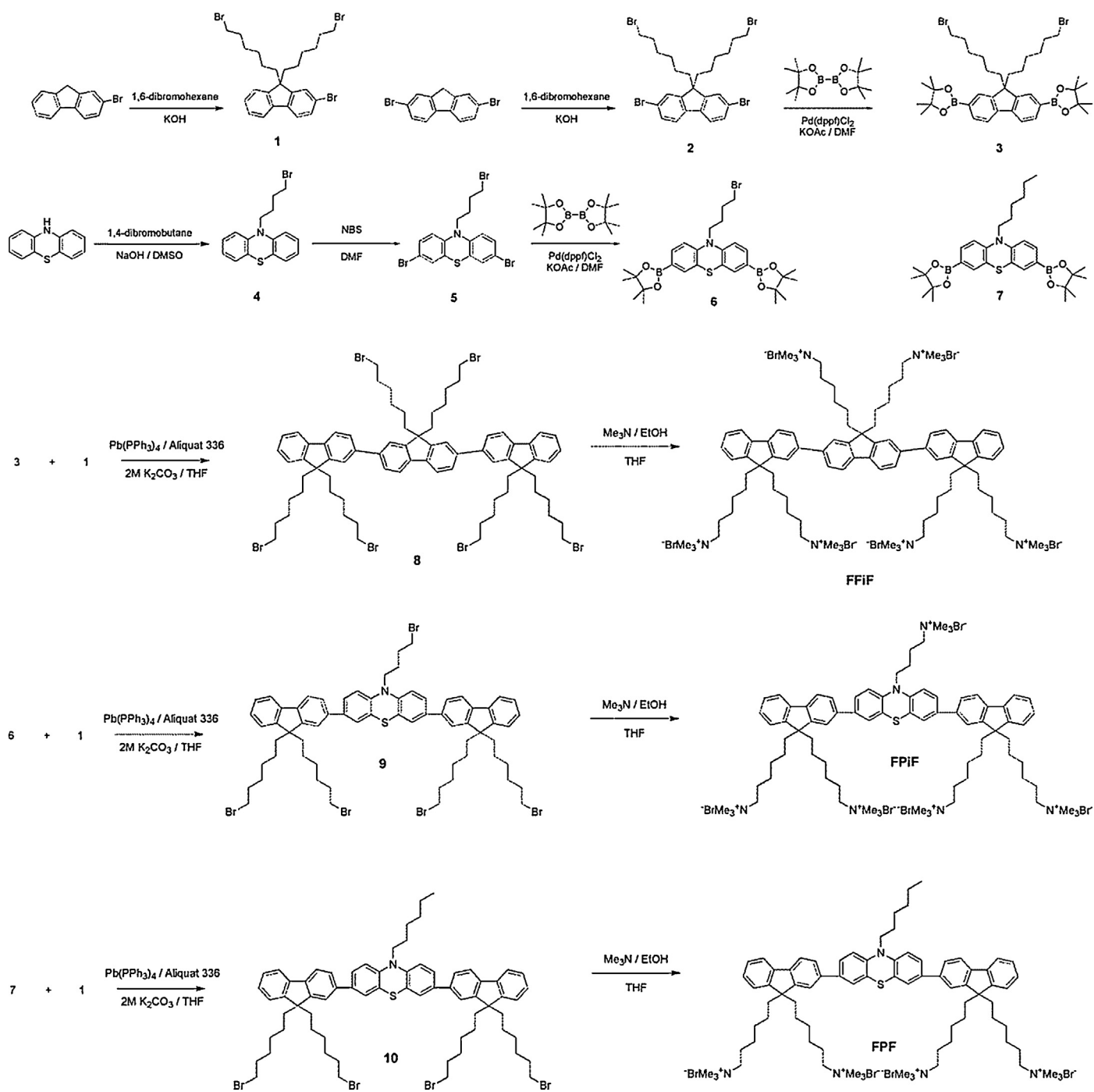
## 1. Introduction

The practical application of polymer solar cells (PSCs) based on conjugated polymers still have been limited up till now and its low efficiency is one of the barriers. It has encouraged intensive researches in recent years and the performance of PSCs has been rapidly improved by the development of new materials [1–7] and optimization of morphologies by processing methods [8–10]. On the other hand, the interface between the organic material and the electrode is a crucial issue due to charge extraction affects device performance greatly. Good interface properties result in a higher short-circuit current ( $J_{sc}$ ) and a higher open-circuit voltage ( $V_{oc}$ ),

which are the most important factors for solar-cell performance. Therefore, interfacial modification becomes one of the most important research pivotal points. In general, PSCs with conventional device architecture consists of a poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (hole-transporting layer) and a bulk-heterojunction (BHJ) layer sandwiched between a high work function-hole collecting conducting transparent metal oxide electrode (ITO) and a low work function-electron collecting metal electrode (Al) [11]. In order to enhance the electron extraction efficiency from active layer to cathode, a thin buffer layer is introduced between them. In the past, a series of buffer materials such as LiF [12], poly(ethylene oxide) [13],  $\pi$ -conjugated polymer electrolytes [14–17], alcohol-soluble neutral conjugated polymers [18], non-conjugated polymer electrolyte based on viologen derivatives [19], poly(sodium 4-styrenesulfonate) [20], or poly(vinyl alcohol) [21] have been reported. Since the

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**Scheme 1.** Synthesis route of monomers and oligomers FFiF, FPiF, and FPF.

favorable interface dipole formed by interfacial layer, the work function of metal and contact resistance are reduced and these are beneficial for developing power conversion efficiency of PSCs.

Recently, conjugated polyelectrolytes (CPEs) and oligoelectrolytes (COEs) containing a  $\pi$ -delocalized backbone with ionic pendant groups have attracted great interest for interfacial-modification materials [22–26]. Their solubility in polar solvents enables the fabrication of multilayer polymer-based devices by the solution-processing approach and the avoidance of intermixing between the water/alcohol-soluble interlayer and the deposited

organic soluble active layer [17]. It has been reported that the ionic groups at the end of side chains on the polyfluorene back bone-based CPEs induced the formation of favorable interface dipole at the cathode interface which lead to decrease the work function of the cathode. Furthermore, the conformation of polymer backbone also affects the electron injection/collection properties but has not fully demonstrated. By comparing with the CPEs, COEs have advantages over the CPEs in terms of processibility such as synthetic procedure, purification of final product, reproducibility of synthesis and materials scale-up, which can also greatly improve the fabrication reproducibility [27].

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