

# Effect of side chain arrangement of conjugated polyelectrolytes buffer layer on the photovoltaic properties



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## ABSTRACT

Conjugated polymer electrolytes (CPEs) are well known materials for reducing the electron injection/collection barrier at the cathode interface by the formation of favorable interface dipole. Regardless of their potential applications as a cathode buffer layer (CBL), the effect of the arrangement of side chains with ionic groups of CPEs on photovoltaic properties is not yet fully investigated. In this research, a series of cationic CPEs based on phenothiazine and fluorene, poly[9,9-bis(6-(*N,N,N*-trimethylammonium)-hexyl)-9*H*-fluorene] bromide (PHF), poly[9,9-dihexyl-9*H*-fluorene-*alt*-9,9-bis(6-(*N,N,N*-trimethylammonium)-hexyl)-9*H*-fluorene] bromide (PHcoF), poly[10-(4-(*N,N,N*-trimethylammonium)-butyl)-10*H*-phenothiazine-*alt*-9,9-bis(6-(*N,N,N*-trimethylammonium)-hexyl)-9*H*-fluorene] bromide (PTF), and poly[10-butyl-10*H*-phenothiazine-*alt*-9,9-bis(6-(*N,N,N*-trimethylammonium)-hexyl)-9*H*-fluorene] bromide (PTcoF) have been applied as CBL materials to demonstrate how the arrangement of side chains with quaternary ammonium bromide (QAB) influences photovoltaic properties. PHF and PTF have QABs on every side chain; whereas, PHcoF and PTcoF have QABs on the side chains alternatively. According to the DFT calculation, the conformation of backbone based on fluorene (PHF and PHcoF) is expected to be not exactly in a zigzag conformation, while the zigzag conformation is expected for the alternated copolymers based on phenothiazine and fluorene (PTF and PTcoF). Thus, a number of accumulated QABs by the spontaneous rearrangement of side chains of PHF and PTcoF at the surface of Al electrode will be bigger than that of PHcoF and PTF. A larger number of accumulated QABs at the interface between the thin film of CPEs and the Al electrode leads to a bigger net induced dipole moment by the accumulated QABs, indicating a larger reduction of the effective WF of the Al cathode and reduction of a Schottky barrier at the cathode interface. As a result, the performances of PSCs with PHF and PTcoF as a CBL are better than those of the device with PHcoF and PTF.

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## 1. Introduction

Recently, interface modification by introducing a thin layer of polyethylene oxide [1], alcohol-soluble neutral conjugated polymers [2], non-conjugated polymer electrolytes [3,4], non-conjugated polar polymers [5–7], conjugated polymer electrolytes (CPEs) [8–13], zwitter ionic conjugated polymer electrolytes [14], and non-conjugated small-molecule electrolytes [15] as a cathode buffer layer (CBL) have been demonstrated for achieving better power conversion efficiency (PCE) of polymer solar cells (PSCs). These materials enable fabrication of devices by the solution process without damaging the underlying layer because these are soluble in aqueous or aqueous alcoholic solvent. So far, polyfluorene

(PF)-based CPEs have been mainly reported for solution processible CBL. Although the operating mechanism of CPEs as a CBL has not yet been clearly demonstrated, one plausible reason for enhancing the PCE in the devices using CPEs as a CBL is that the work function (WF) of the cathode can be reduced by the formation of favorable interface dipole at the cathode interface by the ionic groups at the end of the side chains. Ionic components of the PF based-CPE are accumulated at the top of the CPE surface owing to the presence of a repulsive interaction between the ionic groups and the hydrophobic semiconducting organic layer, indicating that the spontaneous organization of CPEs occurs during the spin coating process [16(a)]. Thus, there will be a redistribution of the internal electric field in the device and the formation of permanent dipole through the spontaneous reorientation of the ionic functional groups of CPEs at the surface of a semiconducting polymer layer.

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Oh et al. [10] reported that PF-based CPE with both quaternary ammonium bromide (QAB) and ethylene oxide side groups on the 9-position of fluorene moiety (PF-oxy-F) induce very large interfacial dipoles at the cathode interface. Thus, the PCE of P3HT (poly(3-hexylthiophene)):PCBM ((6,6)-phenyl-C61-butyric acid methyl ester) based PSC with Al as a cathode reaches 3.89%. The performances of the device were dependent on the length of the ethylene oxide side chain, as well, because a longer ethylene oxide chain induces a larger interface dipole compared to that of the polymer with shorter ethylene oxide chain. This may be possible because of the conformation of the PF backbone, which does not have an exact zigzag arrangement. According to the theoretical study of the conformation of PF backbone, neighboring fluorene units typically form dihedral angles ranging from 15° to 24° [17], which means that the alkyl side chains on the 9-position of fluorene rings do not have an exact zigzag conformation along the backbone [18]. In a similar way, the work function of the cathode can be tuned by the number of ionic functionalities in CPE [19].

Although CPEs are the potential materials for a CBL in PSCs, the effect of the conformation of CPEs backbone on the electron injection/collection properties is not yet fully demonstrated. In this paper, cationic CPEs with QAB (Fig. 1) at the end of the side chain, which are poly[9,9-bis(6-(*N,N,N*-trimethylammonium)-hexyl)-9*H*-fluorene] bromide (PHF), poly[9,9-dihexyl-9*H*-fluorene-*alt*-9,9-bis(6-(*N,N,N*-trimethylammonium)-hexyl)-9*H*-fluorene] bromide (PHcoF), poly[10-(4-(*N,N,N*-trimethylammonium)-butyl)-10*H*-phenothiazine-*alt*-9,9-bis(6-(*N,N,N*-trimethylammonium)-hexyl)-9*H*-fluorene] bromide (PTF), and poly[10-butyl-10*H*-phenothiazine-*alt*-9,9-bis(6-(*N,N,N*-trimethylammonium)-hexyl)-9*H*-fluorene] bromide (PTcoF) were synthesized to investigate how the conformation of backbone and a number of QABs on the side chains by the conformation change of the polymer backbone influence photovoltaic properties. As shown in Fig. 1, the alternate copolymers in this study have different structural features. PHT and PTF have QABs on every side chain; whereas, PHcoF and PTcoF have QABs on the side chain alternatively. The arrangement of side chains of the copolymers will affect the effective WF of the cathode and the wettability of CPEs on the surface of the organic semiconducting layer. The PCE of the device with PHF and PTcoF as a CBL were 3.25% and 3.29%, respectively, which were higher than those of the devices with PHcoF and PTF (2.99% and 3.13%, respectively).

Thus, the spontaneous organization of ionic groups (QABs) on the side chains of PF-based CPEs along with the conformation of backbone would be an important factor for affecting the PCE of PSCs.

## 2. Results and discussion

### 2.1. Theoretical study of conformation of CPEs

Fig. 2 presents DFT-optimized geometries and their calculated energies of oligo(9,9'-dihexylfluorene) (F) and alternated oligomers of *N*-butylphenothiazine (PT) and 9,9'-dihexylfluorene (F). The energy difference between the arrangements of side chains in an alternated (zigzagged) way (denoted as ND) and the other (denoted as D) with respect to the backbone shows quite interesting features. Here, we compare the energy of the two conformations mentioned above. When the repeating unit of the polymers is increased, the energy difference ( $\Delta E$ ) is increased. Just as the  $\Delta E$  between ND and D conformation for F-dimer and tetramer were increased from 0.006 to 0.084 kcal/mol, the value for F-PT dimer and tetramer were increased from 0.122 to 0.322 kcal/mol. It is certain that this trend will be valid for further calculations with the addition of more repeating units. Based on this, we compared the energy difference between PF and F-PT polymers, suggesting that ND conformation is more preferred for F-PT polymer because the energy difference for the polymer based on F-PT will be bigger than that of PF. The difference would be much greater if more repeating units were considered in the calculations. As for PF, the neighboring F units would not be aligned exactly in ND or D arrangement along the backbone due to the small  $\Delta E$ , which is consistent with the previous theoretical study for the conformation of PF backbone [17,18]. On the contrary, the ND conformation of alternated co-oligomers comprising phenothiazine-fluorene is more stable than the arrangement of D with a relatively substantial energy difference; thus, the zigzag arrangement is preferred here.

Park et al. [16(a)] examined the molecular orientation and composition of 10 nm thick PF based-CPE film on top of 80 nm-thick MEH-PPV film by NEXAFS. PF based-CPE reveal mild plane-on (face-on) orientation (i.e. not perfect face-on orientation but tilted orientation). However, they found that a larger surface

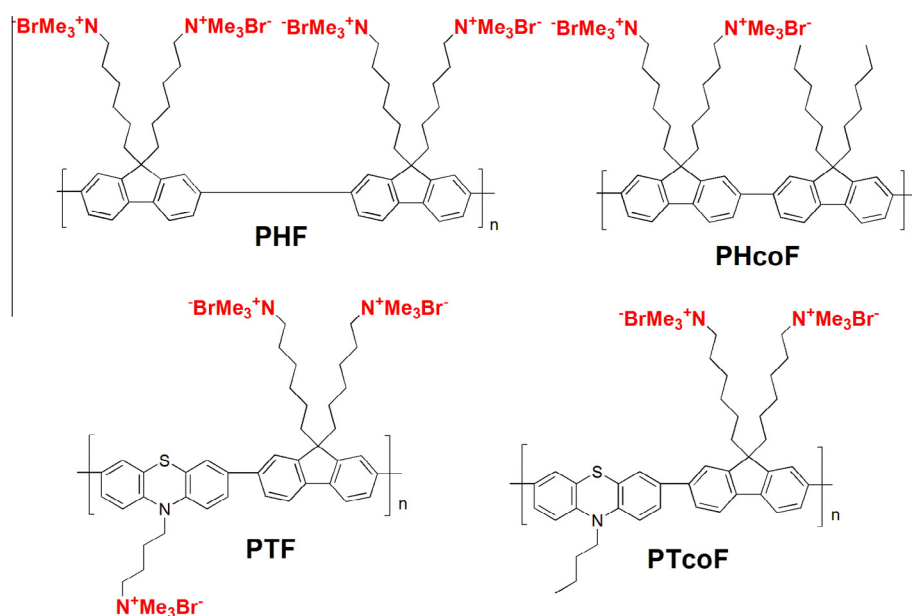


Fig. 1. Chemical structure of CPEs based on fluorene and phenothiazine.

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