

고분자 태양전지를 위한 비공액형 고분자 전해질

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Non-Conjugated Polymer Electrolytes for Polymer Solar Cells

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초 록

고분자태양전지는 용액공정에 의한 생산이 가능하여, 경량, 저비용, 기계적 유연성 및 고효율과 같은 많은 이점이 있다. 이들은 지난 수십 년 동안 많은 관심을 끌어들였다. 공액 고분자 전해질(conjugated polymer electrolyte, CPE) 및 비공액 고분자 전해질(non-conjugated polymer electrolyte, NPE) 재료는 기존의 금속 산화물 중간층과 관련된 일반적인 약점(전하 수집능력 저하 및 금속/고분자 계면에서의 상용성 저하 등)을 극복하기 위해 사용되었다. 그러나 CPE의 합성은 매우 복잡한 합성과정이 필요하며, 대량합성이 어려운 단점이 있다. 따라서 상대적으로 합성이 용이한 NPE를 개발 혹은 기존에 개발되어 있는 NPE를 이용하면 보다 쉽게 단점을 극복할 수 있다. 이온 그룹이 포함되어 있는 경우 NPE는 특히 고분자 태양전지를 구현함에 있어 많은 이점을 제공할 수 있으며, 이에 본 총설에서는 그 동안 개발 혹은 응용되었던 NPE에 대한 내용을 다루었다.

Abstract

Polymer solar cells have attracted extensive attention over the past decade due to their benefits, such as good solution-processability, light weight, low-cost, mechanically flexibility, and high efficiency. Conjugated (CPE) and non-conjugated (NPE) polyelectrolyte materials have been employed to avoid the typical weaknesses associated with conventional metal oxide interlayers. However, the application of CPEs is more complicated than that of NPEs because the synthesis procedures are complicated. NPEs containing charged ion groups can provide numerous benefits for renewable energy applications. Especially when implemented in polymer solar cells.

Keywords: Polymer solar cell, Non-conjugated polyelectrolyte, Interfacial layer, Organic electronics, Photovoltaic device

1. Introduction

Despite continuous efforts to develop renewable energy sources, they not been able to replace fossil fuels. The initial cost of renewable energy systems, such as photovoltaics, tends to be higher than that of diesel and fossil fuel energy systems. However, photovoltaics is environmentally safe and offers many advantages, including low maintenance and running cost. Previous photovoltaic research predominantly employed inorganic materials, such as inorganic semiconductors and metal conductors. However, over the past several decades, organic and polymer electronic and optoelectronic materials with considerably

cheaper production costs have been applied as solar power and shown promising power conversion efficiencies (PCEs). Polymer solar cells (PSCs) have recently gained significant attention, as they are a promising alternative for fossil fuels that produce sufficient solar energy, are lightweight, have low manufacturing costs, and can be employed in flexible devices[1,8]. PSCs utilize donor polymers that require deep HOMO energy levels, to provide high, open-circuit voltages (V_{oc}), proper LUMO energy levels for efficient charge separation, and a low bandgap for abundant sunlight harvesting[9,11].

Previous studies have confirmed that inorganic metal oxides have been commonly used in interfacial materials due to their solution processability and their electron-selective characteristics, which comes from their conduction band edges that are comparable with the deep valence bands and the LUMO level of fullerene[12,16]. Although, PSCs using metal oxides are limited due to significant annealing temperatures (over 200 °C) being necessary to obtain a crystallinity that resides high

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enough to produce a large charge carrier mobility[12,13]. To improve performance, these devices need a post-UV treatment[14,16]. Due to the high-temperature annealing process, the conjugated polymers can promote a crucial photo-oxidation. This process must be inhibited to support the practical use of PSCs, contrasting with the conventional method that uses flexible, plastic substrates and post-UV treatment effects[17].

To avoid the typical weaknesses hindering metal oxide interlayers, conjugated polyelectrolytes (CPEs) and non-conjugated polyelectrolytes (NPEs) have been used. These polymer-based interlayers modify the work function of ITO by forming very light, interfacial dipoles and promoting charge transport to the ITO electrode[18,22]. PSCs using CPEs have shown better performance than those employing NPEs due to the charged ionic pendant groups in the cationic structure of CPEs, which can produce significantly more powerful dipole moments than the neutral NPEs[20]. However, using CPEs is challenging because their charged ionic groups make their synthesis sensitive and difficult. Cationic NPEs have been used in several research fields, including biology[23], and in layer-by-layer deposition studies[24,25] because of their film formation property of ionic self-assembly onto reversely charged surfaces area. However, materials with NPE structures have not been commonly used in PSCs[17].

Previous studies have shown improvement in PSC performance when non-conjugated polymers, such as poly(4-vinylpyridine) (PVPy) [26,27], poly(2-vinylpyridine)[28], poly(sodium 4-styrenesulfonate)[29], poly(4-vinylpyrrolidone) (PVP)[30], poly(4-vinylalcohol)[31], poly(ethylene oxide) (PEO)[32,33], polyacrylonitrile (PAN)[34,39], polyethylenimine (PEI)[40,46], poly[3-(6-trimethylammoniumhexyl)thiophene] (P3TMAHT)[47,48], and tetra-*n*-alkylammonium bromides[49], were used as interfacial layers. Furthermore, dye-sensitized solar cells (DSSCs) and hybrid solar cells have employed NPEs, including poly(oligoethylene methacrylate) (PMEO)[50], poly(propylene oxide) (PPO)[51], polyacrylamide[52], polyallylamine (PAA)[17], poly(methyl methacrylate)[53,54], polysiloxane with quaternary ammonium side groups (PSQAS)[55], poly(4-vinylpyridine)[26], and poly(4-vinyl pyrrolidone) (PVP)[30,56].

This review primarily focuses on the fundamentals and applications of NPEs and is organized as follows: First, we provide a general background on NPEs and introduce the syntheses of various NPE structures. This section also discusses how to prepare the main types of CPE structures and extensively compares the different synthetic approaches. In the second section, we discuss the electronics properties of NPEs and present a comprehensive account of their application in energy fields, particularly as PSCs. The final chapter examines the emerging applications of NPEs in organic optoelectronic devices and details how the NPE molecular structure dictates the most relevant properties of these devices. The readers are encouraged to read this review for basic information and descriptions of the current work in this field of renewable energy research.

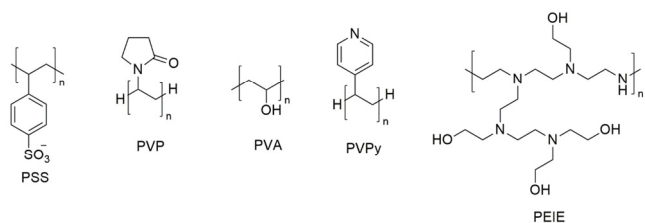


Figure 1. Selected structures of non-conjugated polymers used in organic solar cells.

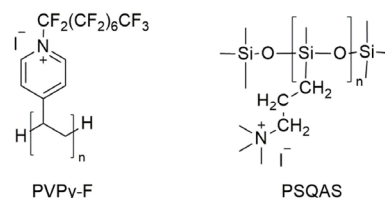


Figure 2. Selected structures of non-conjugated polyelectrolytes (NPEs) used in solar cells.

2. Design and Synthesis of Non-Conjugated Polymer Electrolytes

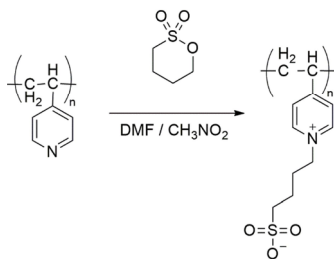
CPEs have attracted increasing attention for their potential to lower the work function of electrodes when used in organic solar cells [47,48,57]. NPEs[41,58] have also demonstrated this potential[59,61]. Several types of modified non-conjugated polymers (Figure 1) have also been developed to produce NPEs.

CPEs have conjugated backbones, which makes their synthesis expensive and may cause external electronic effects. In contrast, NPE syntheses are easy, cheap, and enable ionic groups to be examined without interruption from the backbone.[17,19,62] Hence, NPEs can provide insight into the effects that ionic materials impart on organic solar cell energy bands.

NPEs have attained considerable interest due to their abundant potential for medicinal and biological applications. Furthermore, their synthesis and purification are more straightforward than those of polyelectrolytes with conjugated backbones[17,23,40,63,65]. Despite this, there exist few studies employing NPEs in optoelectronics. Various types of NPEs (Figure 2) were successfully synthesized and applied to solar cells.

Various synthetic pathways have been developed in recent years, resulting in structurally diverse NPE structures. Earlier reports on NPEs mainly detailed poly(sodium 4-styrenesulfonate)[29], PEI, and PAA[17] backbones with ionic functional groups. For example, Br⁻, I⁻, and BIm₄⁺ were used as electrode interlayers to enhance solar cell performance[43]. Another study reported NPEs based on ethoxylated polyethylenimine (PEIE) with PbX₂ (X = I, Br, and Cl) complexes as polymeric analogs of perovskite semiconductors (CH₃NH₃PbX₃)[44].

Lee *et al.* fabricated a non-conjugated, zwitterionic polyelectrolyte based on poly(4-vinylpyridine) (PVPy-ZW) to improve the electron transporting layer. The PVPy-ZW was made by reacting poly(4-vinylpyridine) with butanesultone in nitromethane for 1 day (Scheme 1).



Scheme 1. Synthesis of poly(4-vinylpyridinebutanesulfone) (PVPy-ZW)[26].

The solution was subsequently cooled to room temperature, and the crude product was filtered, washed with diethyl ether, and dried under the vacuum[26]. A similar synthesis was designed to produce poly(4-vinyl N-heptadecafluorooctyl pyridinium iodide) (PVPy-F), where a dimethylformamide/nitromethane solvent system gave the desired product as a solid (72.1%) after 24 h[66].

In 2017, Kim *et al.*[67] prepared a polyelectrolyte with a partially protonated PEI backbone and tetraimadazolylborate anions (PEIBIm₄). They synthesized PEIBIm₄ using the conjugate acid of BIm₄ (HBIm₄) [68]. The solution of PEI was mixed into isopropanol and stirred for 2 h to give the product.

Kang *et al.*[43] reported syntheses where aqueous HBr or HI was added to a PEI solution to give the polyelectrolytes PEIH⁺Br⁻ and PEIH⁺I⁻, respectively. The reactions were complete when aliquots from the reaction mixture had pH values between 5.0 and 5.5. The crude product was precipitated in isopropanol, re-dissolved in anhydrous methanol, and then precipitated again in diethyl ether. The gummy-solid product was obtained after being dried under vacuum. In 2017, Park *et al.*[41] synthesized a series of polyelectrolytes, PEIEH⁺Cl⁻, PEIEH⁺Br⁻, and PEIEH⁺I⁻, from a non-conjugated polymer backbone (PEIE) and various anions (Cl⁻, Br⁻, and I⁻) via acid-base reactions. Aqueous solutions of PEIE (pH ≈ 10) were neutralized with 1 M acids (HCl, HBr, and HI) until the pH reached ≈ 5. The NPE films were then made from the solutions in 2-methoxyethanol via spin-coating.

3. Electronics Properties of Non-Conjugated Polyelectrolytes

The excellent water solubility of NPEs eliminates any adverse environmental effects from their use and allows for tunability of an electrode work function. Previous studies have confirmed that NPEs, specifically PEI and PAA, have been employed in organic solar cells as a cathode buffer layer to enhance efficiency[29,31,63,69,70]. A polarized surface is generated when the NPE decreases the work function, allowing the electrode to productively act as a cathode. In these circumstances, NPEs can improve the collection of active layer electrons by adjusting the LUMO level to that of the cathode Fermi level. This condition can produce an ohmic contact, which leads to efficient device performance[43].

In 2012, Kang *et al.* constructed PEI and PAA and investigated their application in PSCs. The functional amines and the non-conjugated

backbones of these compounds have similar repeating units. Employing functional amines as a cathode interfacial material can improve solar cell performance. This is ascribed to many reasons, the first of which being the water solubility of the NPEs, which is due to the polarity of functional amines and enables solution processing without interference from non-polar solar cell composites. The cationic properties of the functional amines also benefit device performance, as their strong basicity allows them to be partially protonated by water. This produces interfacial dipoles from the cationic NPEs between the ITO cathode and photoactive layer. The electrostatic self-assembly of NPEs occurs when the polyelectrolytes are placed on the ITO electrode surface. The cationic NPEs with amine moieties can actively interact with the terminal oxygen atoms of the ITO surface[25], which later immediately modify the structure of the polymer chains. The ITO surface can vary, where electrostatic interactions stabilize the production of strong dipoles over the NPE and ITO surface interface. Consequently, ITO work function can decrease due to a downward, vacuum-level shift triggered by the surface dipole moments facing away from ITO. This causes the ITO/NPE electrodes to perform as low-work-function cathodes for PSCs[17].

The electronic properties of PVPy-ZW were examined for its application as a cathode buffer layer in organic photovoltaic devices, which were fabricated with either modified or standard PSCs. X-ray photoelectron spectroscopy (XPS) was used to analyze the structure of PVPy-ZW and its addition to ITO or ITO/ZnO surfaces, which showed potential for being able to adjust the work function of the electrodes. This study also conducted Kelvin probe microscopy (KPM) measurements to examine the work function shifts of ZnO and ITO surfaces in the presence of PVPy-ZW. The work function shifts of the electrodes treated with NPE was 4.06 for ITO and 4.05 eV for ZnO. The bare ITO and ZnO surfaces had lower work functions than those of their PVPy-ZW derivatives, indicating that these zwitterionic NPEs can alter electrode work functions. Furthermore, the electron of devices with cathode buffer layer is smaller than that of device with only ITO/ZnO, showing that PVPy-ZW addition can improve device performance[26].

To investigate the effects that NPEs impart on photovoltaic properties, various counterions were introduced to PEI. These NPEs contain protonated, branched PEI backbones with bromide (PEIH⁺Br⁻), iodide (PEIH⁺I⁻) or tetrakis(imidazolyl)borate (PEIH⁺BIm₄⁻) counterions. The surface morphology was characterized by atomic force microscopy (AFM), where pristine ITO substrates displayed homogenous surfaces with a root mean square (RMS) roughness of 1.36 nm. The roughness increased upon the addition of the bromide, the PEIH⁺Br⁻ layer having an RMS roughness of 1.35 nm. The PEIH⁺I⁻ (6.4 nm) deposited on ITO showed an RMS roughness of 6.28 nm, and that of the ITO with PEIH⁺BIm₄⁻ was 1.41 nm. Overall, the surface of the fabricated thin film was even and gave excellent morphological features for organic photovoltaic devices[43].

PEIEH⁺Cl⁻, PEIEH⁺Br⁻, and PEIEH⁺I⁻ are NPE materials that were synthesized from a PEIE backbone with Cl⁻, Br⁻, and I⁻, respectively[41].

Commercially available NPEs, such as poly(sodium 4-styrenesulfonate) (PSS-Na), were employed in the optoelectronic devices. This pol-

yelectrolyte acts as an interlayer at the semiconducting layer or cathode interface. PSS-Na is very soluble in polar protic solvents, and can be applied as an interfacial layer in organic solar cells. When PSS-Na with sodium sulfate salt on the side chain is used, it can lower the work function of an Al (ϕ) cathode coated in a thin layer of NPE, but not that of an Al cathode without NPE. This occurs because beneficial interface dipoles are produced, which were confirmed by ultraviolet photoelectron spectroscopy (UPS) and KPM[29].

Based on previous research, the nanostructures organic photovoltaic cells were designed to reduce charge recombination and maintain exciton dissociation, leading to improved device performance. In 2014, Yuan *et al.* reported a novel NPE: PEIE-Ag composites produced from PEIE. They fabricated the PEIE-Ag nanocomposites by photoexcitation, where the PEIE and AgNO_3 aqueous solution was irradiated with ultraviolet (UV) light until its color changed from colorless to dark brown. This indicated that the Ag^+ ions were completely transformed to Ag nanoparticles. The result was an efficient interfacial layer that could improve the charge transport of inverted PSCs. The PEIE-Ag interlayer is facilely synthesized and possesses many great features, such as excellent water solubility and unique film formation. Furthermore, its work function is tunable and it significantly enhances electron selectivity and conductivity[40,71,74].

4. Applications for Polymer Solar Cells

Despite inorganic materials, such as inorganic semiconductors and metal conductors, being predominantly used in previous photovoltaic research, studies over the past several decades have employed organic or polymer electronic and optoelectronic materials. These have considerably have cheaper production costs and exhibit promising PCEs, giving them the potential for use in solar power applications. Introducing NPEs into PSCs offers new fabrication opportunities and functions. As shown in Figure 3, NPEs function as an efficient way to lower the work function of electrodes by forming dipole layers at the interfaces. This can lead to a notable improvement in PSC performance [17,45,46,58].

Based on a previous report[29], PSCs with a PSS-Na layer incorporated via spin-coating (0.5 mg/mL) provided a PCE of 2.83%, which was 16% larger than that of devices without the addition of polyelectrolyte (Table 1). The increase in J_{sc} of the modified device is what affected its PCE, while the fill factor (FF) of both devices were relatively similar.

The utilization of PEIE as an NPE in the interlayer of organic solar cells was reported by Yuan *et al.* in 2014, where they investigated device performance when PEIE and PEIE-Ag served as interfacial layers. The device with the PEIE interlayer exhibited an increased J_{sc} (15.55 mA/cm^2), V_{oc} (0.77 V), FF (59.3%), and PCE (7.10%) compared to those of the device with only a ZnO layer. However, the device with the PEIE-Ag interfacial layer achieved even better performance than that of the PEIE device, giving a J_{sc} of 16.61 mA/cm^2 , V_{oc} of 0.77 V, FF of 61.0%, and PCE of 7.66% (Table 1). The effect of different active layers on overall solar cell performance was also evaluated. The

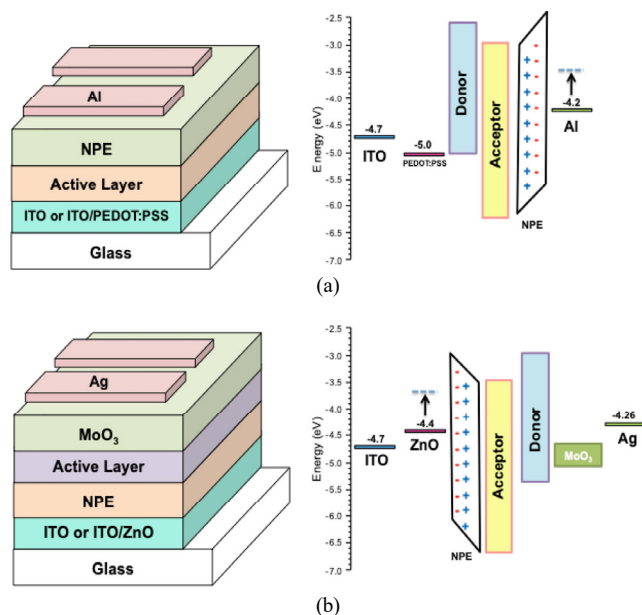


Figure 3. The device structure and the schematic representation of interface dipole by NPEs as interfacial layer in (a) conventional type and (b) inverted type solar cell.

device with PBDTTT-C-T : PC_{71}BM as the active layer showed better device performance than that of the device with P3HT : PC_{61}BM as the active layer, due to its higher PCE and EQE. The thickness variations of PEIE and PEIE-Ag interfacial layers on the devices were also examined, and optimal thickness ranges of 4–8 nm and 15 nm were noted for PEIE and PEIE-Ag, respectively. The results confirmed that the use of PEIE-Ag as an interfacial layer made the device comparatively less sensitive to the thickness. This study also confirmed that PEIE-Ag is a good material for interlayers of organic solar cells and is suitable for commercialization due to its great properties[40].

The photovoltaic properties of the aforementioned PEIH^+Br^- , PEIH^+T^- , and $\text{PEIH}^+\text{BIm}_4^-$ NPEs were also investigated. The fabricated device without the cathode interfacial layers showed a lower PCE (1.05%) than that of the device with the layers. When $\text{PEIH}^+\text{BIm}_4^-$ was applied as the interfacial layer, the PCE was observed to increase as the interlayer thickness increased. This study demonstrates that using a variety of organic cathode interlayers in organic solar cells can result in unique properties emerging from each interlayer, which can lead to specific applications in the device field[43].

A study utilizing PVPy-ZW as the NPE in interfacial layers for either inverted PSCs or conventional PSCs was reported. The interfacial layer could be improved by enhancing the electron extraction ability at the cathode interfaces. Increasing the J_{sc} of a device can enhance its PCE. This was supported by an inverted PSC with NPE exhibiting a higher J_{sc} value (9.06 mA/cm^2) than an inverted PSC without NPE (8.11 mA/cm^2). This outcome can be explained as the transition from a Schottky contact to an Ohmic contact at the cathode interface. The work function of the ITO and the work function of the MoO_3/Ag can be increase by the insertion of a PVPy-ZW layer at the ITO interface, indicating a greater internal electric field in this device than that of the

Table 1. Device Parameters of Polymer Solar Cells (PSCs) with NPEs

NPE	Device structure	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Ref.
PSSNa	Al/NPE/P3HT : PCBM/PEDOT/ITO	0.61	8.58	54.0	2.83	[29]
PEIE	ITO/ZnO/NPE/PBDTTT-C-T : PC ₇₁ BM/MoO ₃ /Ag	0.77	15.55	59.3	7.1	[40]
PEIE-Ag	ITO/ZnO/NPE/PBDTTT-C-T : PC ₇₁ BM/MoO ₃ /Ag	0.77	16.61	61.0	7.66	[40]
PEIE	ITO/ZnO/NPE/P3HT : PC ₆₁ BM/MoO ₃ /Ag	0.61	9.73	65.2	3.87	[40]
PEIE-Ag	ITO/ZnO/NPE/P3HT : PC ₆₁ BM/MoO ₃ /Ag	0.61	10.19	68	4.23	[40]
PEIHBBr	ITO/NPE/PTB7 : PC ₇₁ BM/MoO ₃ /Ag	0.703	15.70	54.2	5.73	[43]
PEIHI	ITO/NPE/PTB7 : PC ₇₁ BM/MoO ₃ /Ag	0.635	15.31	51.5	4.72	[43]
PEIHBIm ₄	ITO/NPE/PTB7 : PC ₇₁ BM/MoO ₃ /Ag	0.710	17.34	55.2	6.59	[43]
P2VP	ITO/ZnO/NPE/PTB7 : PC ₇₁ BM/MoO ₃ /Ag	0.76	15.63	70	8.29	[28]
P2VP	ITO/ZnO/NPE/PTB7-Th : PC ₇₁ BM/MoO ₃ /Ag	0.78	18.36	66	9.54	[28]
P2VP	ITO/ZnO/NPE/PTB7-Th : P(NDI2HD-T)/MoO ₃ /Ag	0.80	12.19	62	6.07	[28]
P2VP ^(a)	ITO/ZnO/NPE/PTB7-Th : PC ₇₁ BM/MoO ₃ /Ag	0.79	21.32	65	10.99	[28]
PVPy-ZW	ITO/NPE/P3HT : PC ₆₁ BM/MoO ₃ /Ag	0.62	9.49	60.4	3.55	[26]
PVPy-ZW	ITO/PEDOT/P3HT : PC ₆₁ BM/NPE/Al	0.62	11.5	48.5	3.45	[26]
PVPy-F	ITO/PEDOT/P3HT : PC ₆₁ BM/NPE/Al	0.62	10.8	51.7	3.46	[66]
PVP ^(b)	ITO/PEDOT : PSS/P3HT : PCBM/NPE/Al	0.61	13.04	49	3.90	[30]
PVP ^(c)	ITO/PEDOT : PSS/P3HT : PCBM/NPE/Al	0.60	11.98	53	3.78	[30]

(a) A VCPT was applied when fabricating the device to maximize light absorption, (b) NPE layer incorporation by spin-coating method, (c) NPE layer incorporation by self-assembly method

device with only ITO/ZnO. Hence, electron collection from the active layer to the cathode is more efficient, leading to a greater J_{sc} value. In contrast, a lower PCE (2.72%) was observed in a device with a PVPy-ZW interlayer than in a device without the polyelectrolyte (2.95%). This was due to the FF of the polyelectrolyte device (50.8%) being smaller than that of the device without the polyelectrolyte (60.6%)[26].

Briefly, PSCs with PEI and PAA materials as cathode interfacial layers were reported in 2013[17]. Both materials contained amine moieties, which gave them both excellent solubility in water. Devices with NPE materials showed high PCEs (around 6.3%), indicating enhanced device performance. In 2016, Shin and co-workers[66] reported another example of the application of NPEs to modify cathode buffer layers. The polyelectrolyte PVPy-F was easily synthesized from poly(4-vinyl pyridine), and upon its implementation in the device an improved PCE of 3.46% was obtained (Table 1).

5. Summary

Various NPEs have attracted significant attention due to their more facile synthesis compared to that of CPEs, and their unique properties can be advantageous to PSC applications. This article has reviewed the design and synthesis pathways of NPEs, their electronic properties, and their application in PSCs. Alongside the development of NPEs, the structure-property relationships of NPEs and their influence on PSC performance warrant further investigation.

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