Organic Electronics 54 (2018) 54–63

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Substituent position engineering of phosphine oxide functionalized triazine-based cathode interfacial materials for flexible organic and perovskite solar cells

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ARTICLE INFO

Keywords:
Cathode interfacial layers
Flexible
Triazine unit
Long-term stability

ABSTRACT

The grand challenge involved in inverted organic solar cell (IOSC) and perovskite solar cell (PSC) technology is to control the interfacial losses at the interface of the photoactive layer with the electron extracting electrode. Herein, three organic small molecules, namely *o*-(F)-PO-TAZ, *m*-(F)-PO-TAZ and *p*-(F)-PO-TAZ, consisting of phosphine oxide (P═O) functionalized 1,3,5-triazine (TAZ) with a fluorine atom (−F) at the ortho (*o*)/meta (*m*)/para (*p*) positions of the phenoxy group attached to the TAZ unit are developed via a rational design approach and used as cathode interfacial layers (CILs) in flexible IOSCs and PSCs. We realized that the −F position particularly affects the glass transition temperature (T_g) of the PO-TAZ derivatives, which in turn exerts a positive effect by maintaining robust and smooth morphological features. This gives the IOSC and PSC devices an −F position-dependent performance. Particularly, ZnO/*p*-(F)-PO-TAZ-based flexible IOSC and PSC devices display not only high power conversion efficiencies (PCEs) of 7.68% and 14.64% but also long-term stability that are superior to those of the control and *o*-(F)- and *m*-(F)-PO-TAZ-based solar cell devices. The current work offers new findings on constructing photoactive (organic or perovskite) layer/CIL interfaces and assists in the rational design of CILs to facilitate efficient photovoltaic devices.

1. Introduction

A highly efficient photovoltaic system capable of converting sunlight into electrical energy will assist in the future development of fully sustainable energy sources. In recent years significant research attention has been devoted to developing cost effective, solution-processible and large area devices for next generation flexible solar cell technologies to meet the demand for clean and inexpensive energy [1–3]. Perovskite solar cells (PSCs) and inverted organic solar cells (IOSCs) display greater promise than do the other photovoltaic devices with power conversion efficiencies (PCEs) surpassing 22.1% and 11%, respectively, by incorporating appropriate cathode interfacial layers (CILs), hole transporting materials (HTMs) for PSCs and photoactive donors for OSCs [4,5].

Besides the contribution from the ideal bulk heterojunction (BHJ) photoactive layer and the perovskite layer in OSCs and PSCs, respectively, the huge efforts made to improve the photoactive layer/electrode interface also largely account for the breakthrough performances. Interface engineering has also contributed significantly to creating ideal interlayers for attaining high PCEs [6,7]. The inclusion of IOSCs and conventional type PSCs in the device structures has accelerated the progress by enhancing the efficient electron collection due to the presence of inorganic metal oxide buffer layers such as zinc oxide (ZnO) and titanium oxide (TiO_2) [8–11]. The photovoltaic performance of IOSCs and PSCs has been further enhanced by introducing interlayers between the photoactive layer and the indium tin oxide (ITO) electrode or metal oxide electron collecting buffer layers [7,12–18]. These CILs establish better physical contacts between the metal oxide buffer layers and photoactive layers that decrease the electrical resistance [19–21]. Further, using these CILs has enabled the work function (WF) of the

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https://doi.org/10.1016/j.orgel.2017.12.017
Received 10 October 2017; Received in revised form 30 November 2017; Accepted 16 December 2017
Available online 16 December 2017
1566-1199/

metal oxide layers and metal electrodes to be significantly shifted, thereby enhancing the PCE due to the considerably improved open-circuit voltage (V_{OC}), fill factor (FF) and short-circuit current density (J_{SC}) [22–26].

Among the numerous CIL materials reported, neutral polar organic small molecules have often been utilized since the dipole moments of self-assembled monolayers forming molecules have been used to improve charge injection that can play a major role in shifting the WF of the ZnO electron transporting layer (ETL) [27,28]. Recently, a simple, inexpensive and neutral polar phosphine oxide functionalized 1,3,5-triazine (PO-TAZ) molecule dissolved in isopropyl alcohol (IPA) as a CIL has been reported to decrease the ZnO WF due to the formation of an interfacial dipole layer at the ZnO/PO-TAZ interfaces [7]. In addition, it has also been reported that various water- and alcohol-soluble conjugated polyelectrolytes and cationic quaternary ammonium-based small molecules can restore the oxygen vacancies existing in the ZnO buffer layers via the inclusion of bromine atoms as pendant groups in the polymer backbone [29–32]. Despite these strong achievements in both PSC and OSC research, very limited research attention has been focused on the applicability of the CILs in flexible devices fabricated on poly (ethylene terephthalate) (PET)/ITO to validate the potentiality of the CILs for IOSCs and PSCs. However, the structure–property relationships between CILs and the PCE remain less understood. This motivates us to investigate new functionalities that can be incorporated into CILs to produce fine tunable optoelectronic properties for both IOSCs and PSCs.

Here, we demonstrate the use of the fluorine (−F) atom substituted at the ortho (*o*-)/meta (*m*-)/para (*p*-) positions of the phenoxy group of PO-TAZ, namely *o*-(F)-PO-TAZ, *m*-(F)-PO-TAZ and *p*-(F)-PO-TAZ, as efficient CILs for both flexible IOSCs and PSCs (Scheme 1). In contrast with *o*-(F)-PO-TAZ and *m*-(F)-PO-TAZ, *p*-(F)-PO-TAZ demonstrated high glass transition temperature (T_g) and thus exhibited robust and stable morphology at the cathode/photoactive layer interface. Consequently, the flexible IOSCs and PSCs fabricated with solution-processed *p*-(F)-PO-TAZ as CIL achieved maximum PCEs of 7.68% and 14.64%, respectively, which are significantly higher than those of the pristine ZnO-based flexible IOSCs and PSCs using a transparent conducting electrode (PET/ITO). The F-substituted PO-TAZ derivatives can be deposited at ambient temperatures without any post treatment, making them very suitable and attractive CILs for flexible optoelectronic devices.

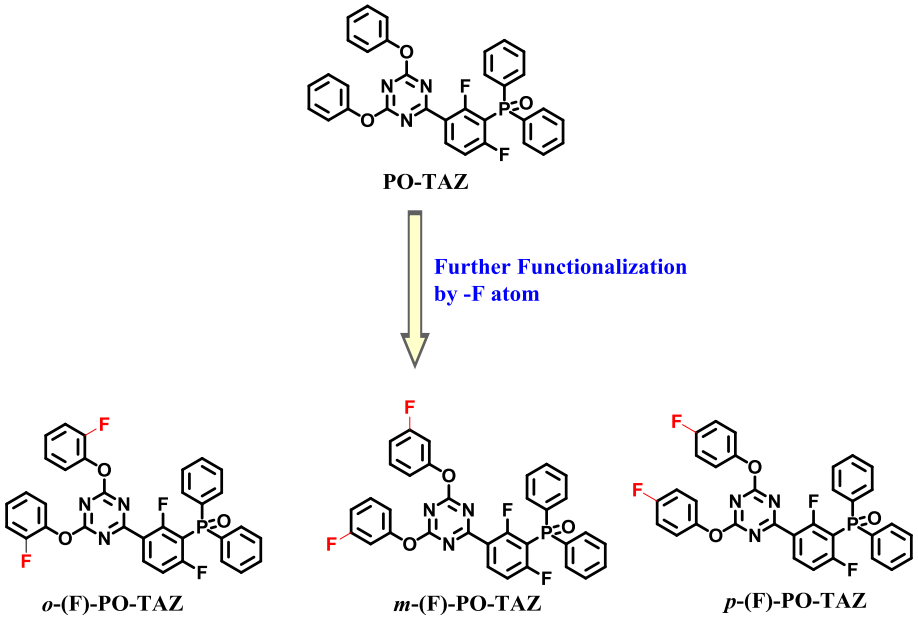
2. Experimental section

2.1. Materials and measurements

All reagents were purchased from Sigma-Aldrich (Korea) and Solarmer (China) and used without further purification. Moisture-sensitive reactions were conducted in a N_2 atmosphere. The other materials were common chemicals and were used as received. ^{1}H NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer (USA) in $CDCl_3$ using tetramethylsilane as an internal reference. The chemical shifts were recorded in ppm related to the singlet of $CDCl_3$ at 7.26 for ^{1}H NMR spectroscopy. The UV–visible absorption spectra were recorded on a JASCO V-570 spectrophotometer (USA). Thermal gravimetric analysis was carried out on a Mettler Toledo TGA/SDTA 851e (Switzerland) under N_2 atmosphere at a heating rate of 10 °C min^{-1} and differential scanning calorimetry (DSC) 822e analyzer under N_2 at a heating rate of 10 °C min^{-1}.

2.2. Device characterization of IOSCs and PSCs

The performances of IOSCs, and PSCs were measured using a calibrated air mass (AM) 1.5 G solar simulator (Oriel Sol3A Class AAA solar simulator, models 94043A (Newport Stratford, Inc.,USA)) with a light intensity of 100 mW cm^{-2} adjusted using a standard PV reference cell (2 cm × 2 cm monocrystalline silicon solar cell, calibrated at NREL, Golden, CO) and a computer-controlled Keithley 2400 (Keithley Instruments, Inc. USA) source measure unit. The external quantum efficiency (EQE) spectrum was measured using an Oriel IQE-200 (Newport Stratford,Inc.,USA) equipped with a 250-W quartz tungsten halogen lamp as the light source and a monochromator, an optical chopper, a lock-in amplifier, and a calibrated silicon photodetector. While measuring the *J–V* curves for the OSC devices, a black mask was used and only the effective area of the cell was exposed to light irradiation. Atomic force microscopy (AFM) was used to measure film thickness, roughness, and surface morphologies in tapping mode acquired with a XE-100 (Park System Corp, Korea). All photoemission measurements were carried out in a PHI-5000 Versa Probe II (ULVAC-PHI, Inc. Japan) ultrahigh vacuum surface analysis system equipped with a He-discharge lamp (21.22 eV) and a monochromatic Al kα X-ray. All spectra were measured at a pressure of 1 × 10^{-6} Pa. Water contact angles were measured using a contact angle 101 measuring system (Plasma systems and materials, Korea).



Scheme 1. Design strategy of the novel F-substituted PO-TAZ derivatives.