CHEMISTRY OF MATERIALS

Effects of Solubilizing Group Modification in Fullerene Bis-Adducts on Normal and Inverted Type Polymer Solar Cells

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Supporting Information

ABSTRACT: Structural control of solubilizing side groups in fullerene-based electron acceptors is critically important to optimize their performance in bulk heterojunction (BHJ)-type polymer solar cell (PSC) devices. The structural changes of fullerene derivatives affect not only their optical and electrochemical properties but also their solubility and miscibility with electron donor polymers. Herein, we synthesized a series of *o*-xylenyl C_{60} bis-adduct (OXCBA) derivatives with different solubilizing side groups to systematically investigate the effects of fullerene derivative structures on the photovoltaic properties of PSCs. The xylenyl side groups on the OXCBA were modified to produce several different OXCBA derivatives in which the xylenyl groups were functionalized with fluorine (FXCBA), nitro (NXCBA), methoxy and bromine (BMXCBA), and phenyl groups (ACBA). End group modifications of OXCBA dramatically affect photovoltaic performance in blend films with poly(3-hexylthiophene) (P3HT),



resulting in power conversion efficiencies (PCEs) ranging from 1.7 to 5.3%. We found that this large range in PCE values is mainly due to differences in the blend morphology and interfacial area of the P3HT:OXCBA derivative films caused by changes in the hydrophobicity of the OXCBA derivatives and their interaction with P3HT. The trend in photovoltaic performance of the different OXCBA derivatives agrees well with those of the interfacial tension, PL quenching, and exciton dissociation probability, which suggests that changes in the interaction with P3HT are largely responsible for their photovoltaic performances. Finally, the OXCBA derivatives were applied in inverted type PSC devices. We note that P3HT:OXCBA blend devices exhibited more than 5% PCE with excellent air stability, which is one of the best inverted type devices based on the P3HT polymer in a simple device architecture without any extra interlayers.

KEYWORDS: electron acceptors, solubilizing groups, fullerene bis-adducts, interfacial tensions, polymer solar cells

1. INTRODUCTION

The current state-of-the-art polymer solar cells (PSCs) are of a type known as bulk heterojunction (BHJ), which consists of a simple mixture of the electron donating conjugated polymers and electron accepting soluble fullerene derivatives.¹⁻⁸ In BHJtype PSCs, an interpenetrating donor-acceptor blend network with a small domain length-scale in the active layer is a critical requirement for enhancing device efficiency because separation of photogenerated excitons can only occur at the donor/ acceptor interface.^{2,9,10} Thus, a nanometer-scale bicontinuous morphology suitable for enhancing exciton separation efficiency is essential for high device performance in PSCs; however, morphology control is not trivial because it is dependent on various parameters affecting both thermodynamic interactions between donor, acceptor, and solvent and morphology development kinetics. In particular, the interaction between electron donor and acceptor is the primary determinant of the phase separation in the blend.

The phase separation behavior in the conjugated polymer donor and fullerene acceptor blend has been intensively studied in terms of structural modification of the conjugated polymers, such as changing the number and length of side chains^{6,11–17} and the substituents on the polymer backbone.^{18–23} Even small changes in a conjugated polymer's structure can change its interaction with electron acceptors, resulting in dramatic differences in blend morphology and solar cell performance.^{24,25} For example, Kim et al. reported that end group modification of P3HT greatly affected the various photovoltaic characteristics of a P3HT/PCBM blend and produced power conversion efficiencies (PCEs) ranging from 2.1% (–OH end group) to 4.5% (–CF₃ end group)).²⁴

Most research to date has focused on structural modification of electron donor polymers. While tuning the chemical

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structure of fullerene derivatives could affect the solubility and miscibility with donor polymers, $^{26-29}$ systematic study of the effects of structural modification of fullerene derivative electron acceptors in PSCs has been very limited. Moreover, smallmolecule fullerene derivatives retain a much higher molecular mobility, resulting in the tendency to diffuse out of the polymer matrix, thus seriously affecting the BHJ blend morphology.^{30–34} Prior investigations have observed that slight modifications of [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) by replacement of the phenyl group with a thienyl group,³⁵ triphenyl amine,³⁶ or fluorene group³⁶ led to significant changes in its solubility and morphology in blend films, resulting in large variations in PCE. Additionally, modification of the aliphatic chain and ester group^{37,38} of PCBM can also influence the lowest unoccupied molecular orbital (LUMO) level and thus the open circuit voltage (V_{OC}) and PCE. However, the underlying reasons for such changes in blend morphology and PCE upon the modification of a fullerene derivative's structure have not yet been clearly demonstrated. Therefore, careful and systematic investigation of the molecular structuredevice function relationship, especially with respect to the structure of fullerene derivatives and its effect on their interaction with electron donor polymers, is essential to establish a design rule for fullerene-based electron acceptors in PSCs.

Of the various types of fullerene-based electron acceptors, we have chosen o-xylenyl C₆₀ bis-adducts (OXCBA) as a model system in which to introduce various end-functionalizations and thereby study the effect of structural changes in the fullerene acceptor. Previous work reported that fullerene bis-adduct electron acceptors effectively can enhance the V_{oc} and PCE because of their higher LUMO levels than that of PCBM.^{39–41} Recently, our group⁴² and another group⁴³ have reported the use of α, α' -dibromo-o-xylene as a building block for the facile preparation of OXCBA. Because OXCBA has a higher LUMO level than PCBM (by 0.17 eV), P3HT:OXCBA devices showed PCE of 5.31% with a $V_{\rm OC}$ of 0.83 V, nearly 50% higher than those of P3HT:PCBM control devices (3.68% with V_{OC} of 0.59 V). In addition to high efficiency, the OXCBA model system has the strong advantages of excellent reaction control and mild reaction conditions, allowing variation in the OXCBA structure (i.e., end group modification of the solubilizing group) by simply tuning the structure of the $\alpha_{,\alpha'}$ -dibromo-o-xylene precursor. The synthetic simplicity and tunability of OXCBA makes it very attractive as a model system for exploration of molecular structure-device function correlations. Furthermore, the effect of end group modification in fullerene bis-adducts, to the best of our knowledge, has not been reported elsewhere.

Herein, we introduce various substituents onto the xylenyl end group of OXCBA to systematically examine the effects of fullerene bis-adduct structural changes on interactions with electron donor polymers and their photovoltaic properties. The structure of OXCBA was carefully modified on the xylenyl group with fluorine, bromine, methoxy, phenyl, and nitro functional groups. Insertion of such functional groups changes the interactions of the fullerene bis-adducts with the P3HT electron donor polymer and thus the P3HT:OXCBA derivative blend morphology, resulting in a range of normal type BHJ-PSC PCEs from 1.7 to 5.3%. We found that the differences were largely caused by changes in the hydrophobicity of the OXCBA derivatives and thus the phase segregation behavior between OXCBA derivatives and P3HT. Direct evidence of changes in the interfacial interaction was provided by measurements of the surface tension of OXCBA derivatives and their corresponding interfacial tensions with P3HT. The results were supported by atomic force microscopy (AFM) and photoluminescence (PL) quenching experiments. In addition, the probability of exciton dissociation in the P3HT:OXCBA derivative PSCs was calculated to monitor exciton dissociation and charge recombination at the P3HT–OXCBA derivative interface, which are in turn significantly influenced by the blend morphology. Finally, we also fabricated inverted type P3HT:OXCBA derivative PSCs, of which the P3HT:OXC-BA-based devices exhibited greater than 5% in PCE with excellent stability, which is among the best simple inverted type P3HT-based PSC PCEs reported to date with basic device structure.

2. RESULTS AND DISCUSSION

2.1. Synthesis. The synthetic scheme and molecular structures of the five different OXCBA derivatives are shown in Scheme 1 (see the Supporting Information for details). 2,3-

Scheme 1. (a) Synthetic Scheme and (b) Molecular Structures of OXCBA Derivatives



Dimethylnaphthalene and three *o*-xylene derivatives functionalized at the 4-position of phenyl ring with fluorine, methoxy, and nitro groups were each reacted with *N*-bromosuccimide (NBS) in the presence of benzoyl peroxide (BPO) in 1,2dichloroethane at reflux to form building blocks for reaction with C_{60} . After purification by silica column chromatography, the synthesized building blocks were verified with ¹H-NMR spectroscopy (see Figure S1 in the Supporting Information).

The various α, α' -dibromo-*o*-xylene derivatives were reacted with C₆₀ using a Diels–Alder reaction procedure previously reported for OXCBA synthesis.⁴² The desired OXCBA derivative products were purified using flash silica column chromatography (hexane/toluene gradient eluent system). The successfully synthesized regioisomeric OXCBA derivatives, 4fluoro-1,2-xylenyl C₆₀ bis-adduct, dihydroanthracyl-based C₆₀ bis-adduct, 1-bromo-2-methoxy-4,5-xylenyl C₆₀ bis-adduct, and 4-nitro-1,2-xylenyl C₆₀ bis-adduct, were confirmed to have over 98% purity by ¹H–NMR spectroscopy, MALDI–TOF mass spectrometry, and elemental analysis (see Figure S1 and S2 in the Supporting Information). For convenience, these four OXCBA derivatives are labeled FXCBA, ACBA, BMXCBA, and NXCBA, as shown in Scheme 1b.

2.2. Electrochemical and Optical Properties of OXCBA Derivatives in Solution. The LUMO levels of fullerene derivatives as electron acceptor are one of the most critical factors in determining the $V_{\rm OC}$ values in PSCs.^{39,44,45} The electrochemical properties of OXCBA derivatives in odichlorobenzene were therefore carefully measured via cyclic voltammetry (CV). The electrochemical properties of these fullerene derivatives are summarized in Table 1 and their CV

 Table 1. Reduction Potentials and LUMO Energy Levels of the Five OXCBA Derivatives

electron acceptors	E_1 (V)	E_2 (V)	$E_{\rm red}^{\rm on}$ (V)	LUMO (eV)
OXCBA	-1.32	-1.70	-1.15	-3.65
FXCBA	-1.25	-1.64	-1.10	-3.70
ACBA	-1.34	-1.72	-1.19	-3.61
BMXCBA	-1.26	-1.64	-1.12	-3.68
NXCBA	-1.26	-1.76	-1.02	-3.78

curves are shown in Figure S3 in the Supporting Information. All OXCBA derivatives exhibit three quasi-reversible reduction waves in the negative potential range between 0 to -2.5 V. As shown in Table 1, FXCBA and BMXCBA exhibited very similar first (E_1) and second (E_2) reduction potential peaks at approximately -1.25 and -1.64 V, respectively; the reduction potential peaks of OXCBA and ACBA were shifted to relatively more negative values when compared with FXCBA and BMXCBA.

The LUMO energy levels of the OXCBA derivatives were estimated from their reduction onset potentials (E_{red}^{on}) . As shown in Table 1, the E_{red}^{on} values of OXCBA, FXCBA, ACBA, BMXCBA, and NXCBA are -1.15, -1.10, -1.19, -1.12, and -1.02 V, respectively, versus a ferrocene standard. Although NXCBA has a LUMO level of -3.78 eV, similar to the LUMO levels of fullerene mono-adducts previously reported (e.g., PCBM and *o*-xylenyl C₆₀ monoadduct at -3.83 eV),⁴² FXCBA and BMXCBA have LUMO values, -3.70 and -3.68 eV, respectively, more similar to that of OXCBA (-3.65 eV). And ACBA had a slightly higher LUMO level (-3.61 eV) than OXCBA. Hummelen et al. previously reported that the LUMO level of PCBM could be influenced by placing electrondonating and electron-withdrawing substituents on its phenyl ring, respectively increasing and decreasing its LUMO level.⁴⁶ Considering these results, the influence of the nitro (NO_2) group of NXCBA, a strong electron-withdrawing group, considerably decreasing the LUMO level from -3.65(OXCBA) to -3.78 eV is easily understandable. Similarly, the slightly decreased LUMO level of FXCBA (-3.70 eV) compared to OXCBA was due to the weak electronwithdrawing characteristics of the fluorine atom. In contrast, the resonance contributed by the additional phenyl ring of ACBA increased the LUMO level (-3.61 eV) from that of OXCBA. Finally, the effect of the methoxy group (a weak electron-donating group) was counterbalanced by that of the bromine atom (a weak electron-withdrawing group), leading to the only slightly decreased LUMO level of BMXCBA (-3.68)eV).

The light absorption ability of the electron acceptors is also of great importance in characterizing their contribution to J_{SC} in PSCs. The visible region absorption spectra (300–800 nm) of OXCBA, FXCBA, ACBA, BMXCBA and NXCBA solutions in *o*-dichlorobenzene are shown in Figure S4 in the Supporting Information. The light absorption properties of the OXCBA derivatives in solution differed very little.

2.3. Photovoltaic Properties of OXCBA Derivatives in Normal and Inverted Type PSCs. To elucidate the relationship between the molecular structure of OXCBA derivatives and the function of PSC devices, we fabricated each normal (ITO/PEDOT:PSS/P3HT:OXCBA derivative/

LiF/Al) type PSC from blends of five different OXCBA derivatives with P3HT, and their performances were measured. The same thermal annealing conditions (5 min at 150 $^{\circ}$ C) were applied to all samples to optimize the device performance. Figure 1a shows the current density–voltage curves of the



Figure 1. Current density–voltage characteristics of BHJ PSCs. P3HT:OXCBA (red), P3HT:FXCBA (blue), P3HT:ACBA (green) P3HT:BMXCBA (orange), and P3HT:NXCBA (black) under AM 1.5 illumination at 100 mW cm⁻²; (a) normal type device architecture and (b) inverted type device architecture.

normal type BHJ solar cells under AM 1.5G illumination with an intensity of 100 mW cm⁻². Each of the devices was prepared under the same conditions, including the P3HT:OXCBA derivative blend ratio (1:0.6 w/w) and solvent concentration. The thicknesses of the P3HT:OXCBA derivative films showed a similar value of approximately 100 nm. The characteristics of the PSC devices are summarized in Table 2 and Table S1 in the Supporting Information. The P3HT:OXCBA device exhibited a PCE of 5.29%, which is comparable to that of our previous report;⁴² however, the P3HT:OXCBA derivative devices showed widely varying PCE values ranging from 1.7 to 5.3%. The performance of the P3HT:OXCBA derivative devices increased in the order NXCBA (PCE = 1.75%), BMXCBA (PCE = 1.84%), ACBA (PCE = 4.27%), FXCBA (PCE = 4.62%), and OXCBA.

Inverted type PSCs present advantages over those with a normal geometry; for example, the inverted type PSCs is required to be able to use roll-to-roll casting to deposit all layers

Table 2. Normal and Inverted Type BHJ PSC CharacteristicsBased on P3HT:OXCBA Derivatives (1:0.6 weight ratio, AM1.5G conditions)

active layer (w/w)		$V_{\rm OC}\left({\rm V} ight)$	$J_{\rm SC}~({\rm mA~cm^{-2}})$	FF	PCE (%)
normal type	OXCBA	0.84	10.53	0.60	5.29
	FXCBA	0.77	10.52	0.57	4.62
	ACBA	0.86	9.64	0.52	4.27
	BMXCBA	0.74	5.88	0.42	1.84
	NXCBA	0.55	7.35	0.43	1.75
inverted type	OXCBA	0.82	9.78	0.63	5.05
	FXCBA	0.74	9.05	0.59	3.95
	ACBA	0.82	8.65	0.55	3.89
	BMXCBA	0.66	4.30	0.53	1.51
	NXCBA	0.57	4.12	0.60	1.41

onto flexible substrates by solution processing, enabling commercial high-speed mass production.⁴⁷ In addition, because of the relatively lower surface tension of polymer donor (i.e., P3HT) compared with fullerene acceptors, the vertically phase-separated morphology in inverted type devices is generally more favorable to the transportation of free charge carriers to their respective electrodes than in normal type devices.⁴⁸ For these reasons, inverted (ITO/ZnO/P3HT:OXC-BA derivative/PEDOT:PSS/Ag) type PSCs were also fabricated. The device characteristics are shown in Figure 1b and Table 2. Similar to the normal type PSCs, the inverted type PSCs showed large variations in the PCE values, which ranged from 1.4 to 5.1%. Interestingly, the performance of inverted type P3HT:OXCBA derivative devices increased in the same order that the normal type PSC device did. The performance of inverted type device increased in the order NXCBA (PCE = 1.41%), BMXCBA (PCE = 1.51%), ACBA (PCE = 3.89%), FXCBA (PCE = 3.95%), and OXCBA (PCE = 5.05%). The electrical, optical and morphological differences of OXCBA, FXCBA, ACBA, BMXCBA, and NXCBA in blends with P3HT will be discussed in the following section to elucidate the reason for the changes in the photovoltaic parameters in each device. Of particular interest is the PCE greater than 5% shown by the P3HT:OXCBA inverted type PSC. To the best of our knowledge, this is the highest PCE reported to date for polythiophene:fullerene inverted PSCs with a basic architecture (ITO/electron transporting layer/active layer/hole transporting layer/anode) without any further modifications.⁴⁹⁻⁵¹

2.3.1. Effects of OXCBA Derivatives on the Fill Factor. As shown in Table 2, both normal and inverted type P3HT:OXCBA derivative devices showed similar trends in their $V_{\rm OC}$ and $J_{\rm SC}$ values, but not the FF values. While an increase in FF values was observed for all P3HT:OXCBA derivative inverted geometry compared with those in the normal geometry, the FF values of P3HT:BMXCBA and P3HT:NXCBA devices were the most significantly improved, from 0.42 to 0.53 and from 0.43 to 0.60, respectively. It is wellknown that the difference in surface tensions between P3HT and PCBM causes a vertical concentration gradient in normal geometry PSCs varying from PCBM-rich near the bottom PEDOT:PSS interface to P3HT-rich near the top air surface.⁵² The preformed PCBM aggregates and resulting P3HT crystallites thus form percolation pathways for both carriers with a vertical phase-separated morphology favorable in particular to the inverted structure.⁴⁸ Therefore, to gain insight into the increasing FF numbers in the inverted type PSCs, the

surface tensions of five different OXCBA derivatives and P3HT were obtained by contact angle measurements. The contact angles of two different solvents (water and glycerol) on the OXCBA derivative and P3HT films were measured and compared (Table 3 and Figure S5 in the Supporting

Table 3. Contact Angle of Water and Glycerol and Surface Tension of OXCBA Derivatives and P3HT

electron acceptors	$\theta_{\mathrm{water}} \; (\mathrm{deg})$	$\theta_{\mathrm{GL}}~(\mathrm{deg})$	surface tension (mN $m^{-1})$
P3HT	98.2	93.2	20.1
OXCBA	91.1	77.8	27.8
FXCBA	88.6	76.7	28.1
ACBA	88.2	72.6	31.1
BMXCBA	87.4	71.7	31.6
NXCBA	86.1	69.3	33.2

Information). From contact angle data, the surface tension of different OXCBA derivatives can be calculated using the Wu model.⁵³

$$\gamma_{\text{water}}(1 + \cos \theta_{\text{water}}) = \frac{4\gamma_{\text{water}}^{d}\gamma^{d}}{\gamma_{\text{water}}^{d} + \gamma^{d}} + \frac{4\gamma_{\text{water}}^{p}\gamma^{p}}{\gamma_{\text{water}}^{p} + \gamma^{p}}$$
(1)

$$\gamma_{\rm GL}(1 + \cos\theta_{\rm GL}) = \frac{4\gamma_{\rm GL}^{\rm d}\gamma^{\rm d}}{\gamma_{\rm GL}^{\rm d} + \gamma^{\rm d}} + \frac{4\gamma_{\rm GL}^{\rm p}\gamma^{\rm p}}{\gamma_{\rm GL}^{\rm p} + \gamma^{\rm p}}$$
(2)

$$\gamma^{\text{total}} = \gamma^{\text{d}} + \gamma^{\text{p}} \tag{3}$$

where γ^{total} is the total surface tension of P3HT and an OXCBA derivative; γ^{d} and γ^{p} are the dispersion and polar components of γ^{total} ; γ_i is the total surface tension of the *i* material (*i* = water or glycerol); γ_i^{d} and γ_i^{p} are the dispersion and polar components of γ_i ; and θ is the droplet contact angle (water or glycerol) on the P3HT and OXCBA derivative film.

Table 3 summarizes the measured water and glycerol contact angles on the each OXCBA derivative and pristine P3HT films. Each OXCBA derivative film shows a different water contact angle (OXCBA (91.1°), FXCBA (88.6°), ACBA (88.2°), BMXCBA (87.4°), and NXCBA (86.1°)) and a corresponding increase in hydrophobicity in the order NXCBA, BMXCBA, ACBA, FXCBA, and OXCBA. The same trend was observed for glycerol contact angles; the surface tensions of the OXCBA derivatives were also calculated and are compared in Table 3. The surface tensions of OXCBA derivatives decreased in the order NXCBA, BMXCBA, ACBA, FXCBA, and OXCBA, ranging from 33.2 to 27.8 mN m⁻¹. Among the five OXCBA derivatives, the surface tension of BMXCBA and NXCBA (31.6 and 33.2 mN m⁻¹, respectively) are higher than those of OXCBA and FXCBA (27.8 and 28.1 mN m⁻¹, respectively). For comparison, the surface tension of a P3HT film was also determined, 20.1 mN m⁻¹, which agrees well with the literature value.^{54,55} Because the surface tension of P3HT is lower than that of all of the OXCBA derivatives, the P3HT and OXCBA derivative materials are expected to preferentially segregate toward the top air surface and the bottom of the active layer, respectively. This vertical phase separation leads to higher FF values in the inverted type geometry for all P3HT:OXCBA derivatives. In addition, the larger surface tension difference between P3HT and OXCBA derivatives in P3HT:BMXCBA and P3HT:NXCBA films provides a clear explanation for the significantly larger enhancement in the FF values of the inverted type PSCs. (from 0.42 to 0.53 for P3HT:BMXCBA

and from 0.43 to 0.60 for P3HT:NXCBA devices) For example, a stronger vertical segregation of P3HT and NXCBA can be expected with NXCBA accumulated at the bottom (ZnO) surface and P3HT at the air surface, where the existence of a fullerene packing layer near the ZnO surface prevents charge carrier recombination and facilitates electron transport, thus leading to a higher *FF*. To find direct evidence of the vertical composition profile of P3HT:OXCBA derivative films, depth profile measurements using dynamic secondary ion mass spectrometry is under investigation.

2.3.2. Effects of OXCBA Derivatives on the Blend Morphology with P3HT. The interfacial tensions (γ) between the P3HT and the OXCBA derivatives provide direct information about the miscibility of the electron donor and acceptor components and their morphological behavior in blend films.⁵⁶ In this regard, the γ values between P3HT and each OXCBA derivative were carefully calculated using the following equation:⁵⁷

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p}$$
(4)

where γ_{12} is the interfacial tension between P3HT (1) and each OXCBA derivative (2); γ_i is the surface tension of the *i* material (*i* = 1 or 2); and γ_i^{d} and γ_i^{p} are the dispersion and polar components of γ_i calculated using the contact angle with water and glycerol (see Figure S5 in the Supporting Information).

The change of end group structure in the OXCBA derivatives derives the significant change in the γ value between P3HT and the OXCBA derivatives. In particular, two materials with a low γ value could minimize the energy penalty required to create a well–mixed interpenetrating network of donors and acceptors with a large interfacial area. As shown in Table 4, the interfacial

Table 4. Calculated Interfacial Tension (γ) between P3HT and Each OXCBA Derivative

tensions of OXCBA and FXCBA in blends with P3HT ($\gamma = 4.1$ and 3 mN m⁻¹) are much smaller than those of BMXCBA and NXCBA in blends with P3HT ($\gamma = 6.3$ and 7.3 mN m⁻¹). The miscibility and blend morphology of P3HT and each OXCBA derivative should thus be distinguishable from one another. For instance, even under the same device processing conditions, the P3HT:BMXCBA and P3HT:NXCBA blends (those with higher γ values) should have a less homogeneous morphology with smaller interfacial area, which would suppress donor–acceptor charge transfer and exciton dissociation at the interface. In contrast, P3HT:OXCBA and P3HT:FXCBA (those with lower γ values) could have potential to form a relatively better-mixed donor/acceptor morphology.

To gain direct evidence of change in the interfacial tension for different P3HT/OXCBA derivative blend films, we investigated the surface morphology of the active layer by tapping-mode atomic force microscopy (AFM). Figure 2a-e show P3HT blended with OXCBA, FXCBA, ACBA, BMXCBA, and NXCBA, respectively, prepared under conditions identical to those used for the optimized BHJ devices. These images reveal significant differences in morphology upon changes in the OXCBA derivative end groups. Panels a and b in Figure 2 clearly show that both the P3HT:OXCBA and P3HT:FXCBA films display relatively better-mixed morphologies at a finer length scale of 20-30 nm. We believe that these morphological advantages in P3HT:OXCBA and P3HT:FXCBA blends contributed to the increase in J_{SC} and FF in BHJ PSC devices, producing better overall photovoltaic performance. In contrast, both P3HT:BMXCBA and P3HT:NXCBA films (Figure 2d, e) with higher γ values of 6.3 and 7.3 mN m⁻¹, respectively, display poor morphologies with a larger domain size. In addition, they exhibited relatively very rough surfaces when compared with P3HT:OXCBA and P3HT:FXCBA films. rms surface roughnesses of the P3HT:OXCBA and P3HT:FXCBA films were 0.98 \pm 0.11 and 1.33 \pm 0.25 nm, respectively, whereas those of P3HT:BMXCBA and P3HT:NXCBA films were 6.37 ± 1.04 and 7.72 ± 0.88 nm, respectively. From these results, we note that the trend in the rms roughness measured via AFM in P3HT:OXCBA derivatives is consistent with the trend in calculated interfacial tension values. Consequently, it is believed that the limited interfacial area in the P3HT:BMXCBA and P3HT:NXCBA films results in reduced photovoltaic performance. In contrast, the small interfacial tension in P3HT:OXCBA and P3HT:FXCBA films produced a relatively well-mixed donor/acceptor blend, which facilitates efficient exciton diffusion and charge transfer. Thus, morphological differences within each P3HT:OXCBA derivative film can affect charge separation and charge transfer ability between P3HT and OXCBA derivatives. $^{\rm 58-60}$

To support the morphological trends of P3HT:OXCBA derivative blend films, steady-state photoluminescence (PL) measurements were performed, which provide useful information on the charge (i.e., electron) transfer from P3HT to the OXCBA derivatives. Figure 3 presents the room temperature PL spectra obtained with an excitation wavelength of 460 nm and Table 5 summarizes the PL quenching efficiency of each P3HT:OXCBA derivative blend film. The P3HT:OXCBA derivative blend samples were prepared by spin-coating on glass substrates under optimized device conditions. The fluorescence spectrum of a pristine P3HT film was measured as a control sample. The PL quenching efficiency of different P3HT:OXCBA derivative films was determined by comparing the PL intensity from each P3HT:OXCBA derivative blend film to the PL intensity of the pristine P3HT film. The PL spectra in Figure 3 indicate dramatic PL quenching in P3HT:OXCBA when compared with the P3HT:FXCBA, P3HT:ACBA, P3HT:BMXCBA, and P3HT:NXCBA films. P3HT:OXCBA emission was quenched by 82% relative to pristine P3HT but P3HT:FXCBA and P3HT:ACBA were quenched slightly less, by 76% and 75%, respectively. Furthermore, the PL quenching efficiencies of P3HT:BMXCBA and P3HT:NXCBA were significantly reduced, to 55% and 66%, respectively. These dramatically decreased PL quenching abilities indicate that very poor charge transfer takes place through the interface in the P3HT:BMXCBA and P3HT:NXCBA films.^{24,61-63} This PL quenching efficiency trend between P3HT and OXCBA derivatives is consistent with the trends in the blend morphology and γ values. The intermixed blend morphology with a smaller length scale produces a greater interfacial area, which allows for efficient charge transfer between the donor and acceptor domains.



Figure 2. AFM height images (top line) and phase images (bottom line) of the blend films of P3HT with each OXCBA derivative: (a) OXCBA, (b) FXCBA, (c) ACBA, (d) BMXCBA, and (e) NXCBA. The scale bar is 500 nm. rms roughness: (a) 0.98 ± 0.11 nm, (b) 1.33 ± 0.25 nm, (c) 4.74 ± 0.16 nm, (d) 6.37 ± 1.04 nm, and (e) 7.72 ± 0.88 nm.



Figure 3. Static PL spectra for P3HT (black), P3HT:OXCBA (red), P3HT:FXCBA (blue), P3HT:ACBA (green), P3HT:BMXCBA (orange), and P3HT:NXCBA (purple) films.

Table 5. Calculated PL Quenching Efficiency forP3HT:OXCBA Derivatives

electron acceptors	$I_{\rm film}/I_{\rm P3HT}$	$1-(I_{\rm film}/I_{\rm P3HT})$	quenching eff. (%)
OXCBA	0.184	0.816	81.6
FXCBA	0.235	0.765	76.5
ACBA	0.250	0.750	75.0
BMXCBA	0.451	0.549	54.9
NXCBA	0.336	0.664	66.4

To further explore the effects of the OXCBA derivative end group modification on the BHJ PSCs, the maximum exciton generation rate (G_{max}) and exciton dissociation probabilities [P(E,T)] were measured and compared for different P3HT:OXCBA derivative devices. Each device was biased by sweeping from +1 to -10 V and the saturation photocurrent density (J_{sat}), G_{max} , and P(E,T) were successfully calculated using a published literature method.⁶¹ Figure 4a reveals the dependence of the photocurrent density (J_{ph}) on the effective voltage (V_{eff}), recorded under illumination at 100 mW cm⁻², for our P3HT:OXCBA derivative devices. The values of J_{ph} and V_{eff} can be determined by the following equations:



Figure 4. (a) Photocurrent density $(J_{\rm ph})$ and (b) exciton dissociation probability $(P({\rm E},{\rm T}))$ plotted as a function of effective bias $(V_{\rm eff})$ in P3HT:OXCBA derivative devices.

$$J_{\rm ph} = J_{\rm L} - J_{\rm D} \tag{5}$$

$$V_{\rm eff} = V_0 - V_a \tag{6}$$

where $J_{\rm L}$ and $J_{\rm D}$ are the current densities under illumination and in the dark, respectively, V_0 is the voltage when $J_{\rm ph} = 0$, and $V_{\rm a}$ is the applied voltage. In the high $V_{\rm eff}$ regime, $J_{\rm ph}$ becomes saturated and independent of the bias and temperature and determines J_{sat} . Assuming that all of the excitons become dissociated and contribute to the current in the saturated region,

$$J_{\rm sat} = qG_{\rm max}L\tag{7}$$

where *q* is the electronic charge and *L* is the thickness of the active layer. Because only a portion of the excitons can be dissociated into free carriers under applied voltage, J_{ph} can be expressed using P(E,T)

$$J_{\rm ph} = q G_{\rm max} P({\rm E}, {\rm T}) L \tag{8}$$

As summarized in Table 6, the G_{max} of different P3HT:OXCBA derivative devices showed similar trends to the J_{SC} values. For

Table 6. Maximum Exciton Generation Rate (G_{max}) and P(E,T) for P3HT:OXCBA Derivative Devices

electron acceptors	$ \substack{J_{\rm sat} \\ ({\rm A}\ {\rm m}^{-2}) } $	$\underset{\left(m^{-3}s^{-1}\right)}{\overset{G_{max}}{s^{-1}}}$	P(E,T) under SC condition (%)
OXCBA	149	7.75×10^{27}	80.3
FXCBA	145	7.54×10^{27}	78.0
ACBA	120	6.24×10^{27}	75.9
BMXCBA	117	6.09×10^{27}	54.9
NXCBA	104	5.41×10^{27}	69.4

example, the $G_{\rm max}$ of the P3HT:BMXCBA and P3HT:NXCBA devices (6.09 × 10²⁷ and 5.41 × 10²⁷ m⁻³ s⁻¹, respectively) with lower $J_{\rm SC}$ values exhibited relatively lower $G_{\rm max}$ values compared with the P3HT:OXCBA and P3HT:FXCBA devices (7.75 × 10²⁷ and 7.54 × 10²⁷ m⁻³ s⁻¹, respectively) having higher $J_{\rm SC}$ values. Because the $G_{\rm max}$ value is a measure of the maximum number of absorbed photons, the light absorption ability of P3HT:OXCBA derivative films can be dependent upon the structures of the OXCBA derivatives. The thin-film UV–vis absorption spectra of the P3HT:OXCBA derivative blend films fabricated under optimal device conditions were therefore measured.

As shown in Figure 5, the intensity of the peaks at 550 and 610 nm in the UV-vis absorption spectra was gradually



Figure 5. UV-vis absorption spectra of the blended thin films of OXCBA, FXCBA, ACBA, BMXCBA, and NXCBA with P3HT.

decreased in the order P3HT:OXCBA, P3HT:FXCBA, P3HT:ACBA, P3HT:BMXCBA, and P3HT:NXCBA. The trend agrees well with those of G_{max} and J_{SC} for P3HT:OXCBA derivative films. Interestingly, despite the similar light absorption ability of five OXCBA derivatives (see Figure S4 in the Supporting Information), the UV-vis absorption spectra of each P3HT:OXCBA derivative blend thin film exhibited different 610 nm peak intensities, which originates from highly ordered P3HT chains. Therefore, we suggest that the end group modification of OXCBA was responsible in large part for changes in the degree of P3HT packing in P3HT:OXCBA derivative blend films because differences in the molecular size of OXCBA derivatives and their corresponding intermolecular packing structure could affect the P3HT packing and light absorption properties of the blend film. To compare the molecular size of the OXCBA derivatives, molecular size calculations were performed using the Spartan'08 program and the simulation parameters are shown in Table S2 in the Supporting Information. Because of the existence of various regioisomers in fullerene bis-adducts,⁶⁴ the absolute size difference between OXCBA derivatives cannot be estimated. Instead, we compared the size of the solubilizing group of the different OXCBA derivatives and found that as the molecular size of the OXCBA derivatives increased, the vibronic peaks exhibited lower intensity. For example, addition of the relatively bulkier BMXCBA and NXCBA reduced the peak intensities at 550 and 610 nm.

In addition, the J_{SC} value of PSC devices is influenced by not only the G_{max} value but also the exciton dissociation probability [P(E,T)]. The exciton dissociation probability can be obtained from the normalized photocurrent density (J_{ph}/J_{sat}) . Of particular importance is the P(E,T) value under short circuit conditions ($V_a = 0$ V), which is directly proportional to J_{SC} in the solar cell device. Figure 4b shows the curve of P(E,T)versus V_{eff} (V) in P3HT:OXCBA derivative devices and Table 6 demonstrates that the values of P(E,T) under short-circuit conditions ($V_a = 0$ V) provided a calculated exciton dissociation probability decrease from 80.3% for the P3HT:OXCBA reference device to 78.0, 75.9, 54.9, and 69.4% for the P3HT:FXCBA, P3HT:ACBA, P3HT:BMXCBA, and P3HT:NXCBA devices, respectively. It is worth noting that the trend in exciton dissociation probability for different P3HT:OXCBA derivative films agrees with those of PL quenching efficiency and J_{SC} . Exciton dissociation and charge transfer between donor and acceptor occurs through the interface area, which is mainly determined by the γ value between the donor and acceptor materials. Our result therefore shows that the trend of exciton dissociation probability and PL quenching efficiency matching well with that of γ value is to be expected. In addition, the difference in the dipole moment (see Table S2 in the Supporting Information) of OXCBA derivatives caused by end groups with different dipole moments and polarities may contribute to J_{SC} , specifically due to exciton dissociation and charge recombination.¹⁸ For example, the charge separation would be more difficult for blends of P3HT with BMXCBA and NXCBA, which have end groups containing strong negative charges, because the dissociation of excitons at the interface to produce free electrons can be suppressed by the presence of strongly electronegative end groups in BMXCBA and NXCBA near the interface. Conversely, the end group of OXCBA does not have a negative charge, leading to more efficient exciton dissociation at the P3HT:OXCBA interface.

2.3.3. Effects of OXCBA Derivatives on the Open Circuit Voltage. It is well-known that $V_{\rm OC}$ in BHJ devices is proportional to the difference between the LUMO level of the electron acceptor and the highest occupied molecular orbital (HOMO) level of the electron donor.⁴⁴ For this reason,

changes in the LUMO levels of OXCBA derivatives caused by changes of the end group structure could explain the $V_{\rm OC}$ differences in P3HT:OXCBA derivative devices. In the case of NXCBA, which has a very strong electron-withdrawing group, the LUMO level (-3.78 eV) was significantly lower than that of OXCBA (-3.65 eV). This lower LUMO level resulted in a decrease in the difference between the LUMO level of the fullerene derivative and the HOMO level of P3HT, and thus a significant decrease in the V_{OC} of the P3HT:NXCBA device (0.55 V). Similarly, the introduction of a weak electron withdrawing group (fluorine group) in FXCBA resulted in a slightly reduced LUMO energy level (-3.68 eV) compared to that of OXCBA; accordingly, the P3HT:FXCBA device showed a slightly decreased $V_{\rm OC}$ (0.77 V) when compared with that of the P3HT:OXCBA device (0.84 V). In contrast, the LUMO level of ACBA, which has an additional resonance group (phenyl ring), increased to -3.61 eV, which results in the slightly higher $V_{\rm OC}$ (0.86 V) of the P3HT:ACBA device. For BMXCBA, the competing effects of the electron donating methoxy and the electron withdrawing bromine groups leads to a slight decrease in the LUMO level (-3.68 eV) that explains the decrease in the $V_{\rm OC}$ value.

2.4. Air Stability Measurement in Normal and Inverted Type PSCs. The air stability of PSCs is an important issue for commercialization. In general, inverted geometry PSCs are more stable in air than the normal type structure because their high-work-function metal anodes are resistant to oxidation in air.⁴⁷ Because of its similar excellent device performances in both normal and inverted geometries, we chose the P3HT:OXCBA blend to compare the air stability of inverted type PSCs with that of normal type ones. Figure 6



Figure 6. Air stability tests of normal and inverted type PSCs based on P3HT:OXCBA under ambient condition.

shows the air stability of normal and inverted type PSCs based on P3HT:OXCBA. The initial PCEs of normal and inverted type devices exhibited similar values above 5%. Under ambient atmosphere without any encapsulation, the inverted type PSC exhibited excellent air stability, showing a PCE decrease of less than 0.2% (greater than 95% of the initial PCE value) after 3 weeks of exposure to the air. In contrast, the PCE of the normal type devices dropped to below 50% of the initial value within 2 days and to ~0.5% within 5 days.

3. CONCLUSION

In summary, we synthesized a series of electron acceptors based on OXCBA with various end groups such as fluorine, bromine, methoxy, phenyl, and nitro groups. The changes of end groups in OXCBA derivatives influence their structural and electrical properties. More importantly, by simply varying the end groups, the hydrophobicity of OXCBA derivatives can be easily tuned; this allows systematic control of the miscibility and interfacial interaction with P3HT, which were analyzed by interfacial tension and AFM measurements. As the γ value between P3HT and the OXCBA derivatives decreased, a significant increase in the interfacial area was observed, leading to changes in the PCE ranging from 1.7 to 5.3%. Such control in the interfacial interaction due to end group modification results in increased exciton dissociation and suppressed charge recombination, as shown by increased PL quenching and calculated exciton dissociation probability, producing higher J_{SC} values. In addition, changes in the molecular size of OXCBA derivatives may have some contribution to the P3HT and fullerene packing and thus the light absorption of the blend films. End group modification of OXCBA significantly changes the surface tension of each of the OXCBA derivatives, which affects the vertical phase-separated morphology in the active layer. Because the high surface tensions of BMXCBA and NXCBA lead to accumulation at the bottom surface, the P3HT:BMXCBA and P3HT:NXCBA inverted type devices showed significantly increased FF values compared with their normal type device. Finally, inverted type P3HT:OXCBA PSC devices exhibited over 5% PCE with excellent air stability. Our work provides a model system for fundamental understanding of the molecular structure-device function relationship, especially with respect to the structure of bis-adduct fullerenes and their interactions with electron donor polymers, and suggests a design rule for fullerene-based electron acceptors in PSCs.

ASSOCIATED CONTENT

S Supporting Information

Materials and methods, detail experimental procedures, and additional data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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