Non-Fullerene Small Molecule Acceptors Containing Barbituric Acid End Groups for Use in High-performance OPVs

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We synthesized two new bithiophene-based small molecules, **TT-BBAR**, and **TT-OBAR**, having butyland octyl-substituted barbituric acid (BAR) groups, respectively, via a well-known synthetic method, the Knoevenagel condensation, in high yield. These small molecules displayed solubilities and thermal stabilities sufficient for the fabricating organic photovoltaic cells (OPVs) and were designed to have relatively low molecular orbital energy levels and act as non-fullerene acceptors (NFAs) for use in OPVs upon introduction of electron-withdrawing BAR groups at both ends. For example, the LUMO and HOMO energy levels of **TT-OBAR** were -3.79 and of -5.84 eV, respectively, clearly lower than those of a polymer donor, PTB7-Th. Importantly, the small molecules featured an energy offset with PTB7-Th sufficient for achieving exciton dissociation. The optical and electrochemical properties of **TT-BBAR** and **TT-OBAR** did not depend on the alkyl chain length. Finally, OPV devices were fabricated in an inverted structure using a solvent process. The power conversion efficiency of **TT-OBAR** (1.34%) was found to be slightly higher than that of **TT-BBAR** (1.16%). The better performance and higher short-circuit current value of **TT-OBAR** could be explained based on a morphological AFM study, in which **TT-OBAR** displayed a more homogeneous morphology with a root-mean-square value of 1.18 nm compared to the morphology of **TT-BBAR** (11.7 nm) induced by increased alkyl chain length.

Keywords: Organic photovoltaic cell, Organic photovoltaics, Non-fullerene acceptor, Barbituric acid

Introduction

Research into organic photovoltaics (OPVs) has progressed significantly. Non-fullerene acceptors (NFAs) composed of donor (D) and acceptor (A) units have been widely reported due to their high power conversion efficiencies (PCEs) exceeding 14%. They have several advantages, including their simple synthesis, strong and broad absorption in the UV-Vis region, and easily tunable energy levels.¹⁻³ Electron-deficient groups, such as rhodanine (RH),4,5 1,3-indandione $(IN),^{6,7}$ and 1,1-dicyanomethylene-3-indanone (CNIN)^{8,9} have been widely used as acceptor units, together with fused-ring-based electron-rich groups, such as carbazole (Cz),^{10,11} fluorene (Flu),^{12,13} indaceno-dithiophene (IDT),^{14,15} and indacenodithienothiophene (IDTT).^{16,17}

Barbituric acid (BAR) has been used as an acceptor (A) unit in NFAs designed for use in OPVs. Sullivan *et al.* reported the use of a BAR-containing electron acceptor to evaporate bilayer OPV devices, in which a PCE of 2.6% was achieved using an inverted configuration and SubPc as the donor.¹⁸ D-A-type organic dyes composed of diphenylamine and BAR as the donor and acceptor units, respectively, were reported by Hosseinzadeh *et al.* for application in dye-sensitized solar cells, displaying a PCE of 1.53%.¹⁹ In 2017, our group reported the synthesis of Cz-BAR and

Flu-BAR, in which electron-rich Cz and Flu cores were end-capped with electron-deficient BAR groups, providing a PCE of 1.57% when combined with poly(3-hexylthiophene) in solution.²⁰

In this work, we synthesized new NFAs, **TT-BBAR**, and **TT-OBAR**, having butyl- and octyl-substituted BARs (BBAR and OBAR, respectively) at both ends of the bithiophene core. The introduction of the appropriate alkyl chains rendered them electron acceptors for application in solution-processable OPVs. The physical properties and film morphologies were investigated to determine the relationship between the alkyl chain length and the physical properties.

Experimental

Materials. The TT-Br, TT-CHO, BBAR, and OBAR were prepared according to procedures described in the literature^{21–24} (Scheme 1, see also the Appendix S1 in Supporting information).

Synthesis of TT-BBAR. TT-CHO (0.11 g, 0.49 mmol) was dissolved in anhydrous chloroform (CF) (20 mL). While stirring, three drop of triethylamine and BBAR (0.53 g, 2.23 mmol) were added, and the mixture was stirred at rt. for 20 h. The reaction mixture was extracted with dichloromethane, washed with water, and dried over



Scheme 1. Synthetic routes to TT-BBAR and TT-OBAR.

magnesium sulfate. After removing the solvent, the crude product was recrystallized from acetone several times to obtain a red powder. Yield: 0.29 g (88%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.64 (s, 2H), 7.81 (d, J = 4.2 Hz, 2H), 7.65 (d, J = 4.1 Hz, 2H), 4.00 (dd, J = 15.3, 7.8 Hz, 8H), 1.66 (qq, J = 15.0, 7.6 Hz, 8H), 1.41 (qq, J = 14.6, 7.3 Hz, 10H), 0.98 (q, J = 7.4 Hz, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 162.20, 161.70, 150.77, 150.40, 147.68, 145.92, 138.20, 126.84, 111.22, 42.26, 41.58, 30.20, 30.15, 20.23, 20.17, 13.82, 13.78. Anal. calc. for C₃₄H₄₂N₄O₆S₂: C, 61.24; H, 6.35; N, 8.40; S, 9.62. Found: C, 61.28; H, 6.39; N, 8.40; S, 9.12.

Synthesis of TT-OBAR. This compound was prepared in the same manner as **TT-BBAR** using TT-CHO (0.09 g, 0.40 mmol), OBAR (0.64 g, 1.82 mmol), and CF (20 mL) to provide a red powder. Yield: 0.30 g (83%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.63 (s, 2H), 7.81 (d, J = 4.4 Hz, 2H), 7.65 (d, J = 4.1 Hz, 2H), 7.81 (d, J = 15.4, 8.1 Hz, 8H), 1.67 (m, 8H), 1.32 (m, 40H), 0.88 (t, J = 6.7 Hz, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 162.41, 161.91, 151.00, 150.57, 147.79, 145.95, 138.51, 126.99, 111.62, 42.73, 41.99, 32.03, 32.02, 29.51, 29.47, 29.45, 29.41, 28.38, 28.31, 27.19, 27.15, 22.84, 14.25. Anal. calc. for C₅₀H₇₄N₄O₆S₂: C, 67.38; H, 8.37; N, 6.29; S, 7.20. Found: C, 67.29; H, 8.40; N, 6.43; S, 7.01.

Results and Discussion

Synthesis and Thermal Properties. The TT-BBAR and TT-OBAR were synthesized via the Knoevenagel condensation of TT-CHO and the alkyl-substituted BAR (BBAR and OBAR) in the presence of a triethylamine catalyst in high yields. The synthetic routes are shown in Scheme 1. TT-BBAR and TT-OBAR were dissolved in common organic solvents, such as CF and chlorobenzene, at concentrations sufficient for fabricating OPV devices. The chemical structures and purities of the two small molecules were verified using EA and NMR spectroscopy (Figures S1 and S2). The TGA results indicated a 5% weight loss (T_{5d}) above 390 °C (Figure 1(a)). Both molecules displayed

thermal stabilities sufficient for use in OPVs. The DSC results indicated that the melting temperatures (T_m) of **TT-BBAR** and **TT-OBAR** were 317 and 203 °C, respectively. The crystallization temperatures were 292 and 177 °C, respectively (Figure 1(b)).

Physical Properties. The electrochemical properties of TT-BBAR and TT-OBAR were monitored by CV (Figure 2 (a)). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were calculated from the equations $E_{\text{HOMO}} = -(E_{\text{onset}}, E_{\text{HOMO}})$ $_{ox} - E_{1/2,Fc} + 4.8$) and $E_{LUMO} = -(E_{onset,red} - E_{1/2,Fc} + 4.8)$ eV. The molecular orbital energy levels of TT-BBAR and TT-OBAR were found to be very similar and independent of the alkyl chain length, as shown in Figure 2(b). The HOMO and LUMO energy levels of TT-OBAR were -5.84 and -3.79 eV, respectively. These values were clearly lower than the HOMO (-5.23 eV) and LUMO (-3.19 eV) energy levels of the well-known low band-gap polymer donor, PTB7-Th. In other words, the molecular orbital energy levels of TT-BBAR and TT-OBAR were efficiently lowered by the introduction of electronwithdrawing BAR end groups. Both small molecules





Figure 2. (a) Cyclic voltammogram and (b) energy diagram $(E_{g,CV} \text{ are shown in parenthesis})$ and UV–Vis absorption spectra of (c) **TT-BBAR** and (d) **TT-OBAR**.

2

Table 1. Phy	sical propert	ties of the sn	nall mole	ecules.						
	λ_{\max} (nm)			$E_{\text{onset}} (\mathbf{V})^a$						
	$T_{\rm m}$ (°C)	T_{5d} (°C)	soln	film	$E_{\rm g,opt}$ (eV, nm)	ox	red	HOMO (eV)	LUMO (eV)	$E_{\rm g,CV}^{b} (\rm eV)$
TT-BBAR	317	390	486	477	2.06 (602)	1.50	-0.54	-5.84	-3.80	2.04
TT-OBAR	203	391	486	480	2.04 (606)	1.50	-0.55	-5.84	-3.79	2.05

^a Onset potentials relative to a Ag/Ag⁺ reference electrode.

 b E_{g,CV} was estimated based on the onset potentials of the oxidation and reduction processes (E_{g,CV} = LUMO – HOMO).

featured energy offsets with the PTB7-Th polymer donor sufficient for exciton dissociation.

The UV-Vis absorption spectra of TT-BBAR and TT-**OBAR** were measured in CF solutions and in as-cast films, as shown in Figures 2(c) and 2(d), respectively. The two small molecules displayed comparable absorption spectra in the solution and film states, with absorption maxima (λ_{max}) at 486 and 480 nm, respectively. Both films showed slightly blue-shifted UV-Vis spectra, suggesting H-type aggregation. The optical bandgaps ($E_{g,opt} = 1240/\lambda_{onset}$) of TT-BBAR and TT-OBAR, calculated from the onsets (λ_{onset}) of the UV–Vis absorption profiles of the films, were also found to be similar (Table 1). These results indicated



Figure 3. J-V curves (left) and EQE spectra (right) obtained from the (a) PTB7-Th:TT-BBAR and (b) PTB7-Th:TT-OBAR blend films.

Table	2.	Photovoltaic	properties	of the	OPV	devices."
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that the two small molecules had comparable molecular orbital energy levels and UV-Vis absorption spectra, indicating that the alkyl chain length of the BAR units did not affect the electrochemical and optical properties. In addition, the UV-Vis absorption spectra of the films did not change after thermal (TA) or solvent vapor annealing (SVA) treatment (Figure S3). The electrochemical or optical properties of the two small molecules are summarized in Table 1.

Organic Photovoltaic Properties. The OPV cells were fabricated using an inverted device configuration comprising ITO/ZnO NPs/PEIE/PTB7-Th:TT-BBAR or TT-OBAR (1:2, CF)/MoO_x/Ag. The current-density versus voltage (J-V) curves were obtained under AM 1.5G illumination, 100 mW/cm². Figure 3 presents the J-V and EQE curves measured from the devices, and photovoltaic properties are listed in Tables 2 and S1. Both small molecule acceptors displayed photovoltaic properties. The device prepared using TT-OBAR showed a better performance (1.34%) compared to TT-BBAR (1.16%). The better performance of the device prepared using TT- OBAR was attributed to the higher J_{SC} than that of **TT-BBAR**. The devices prepared using TT-BBAR and TT-OBAR exhibited similar $V_{\rm OC}$ values as a result of having comparable LUMO levels.

As shown in Figure 3, both devices displayed broad external quantum efficiency (EQE) responses in the range of 350-750 nm. The EQE responses at around 500 and 700 nm overlapped significantly with the UV-Vis absorption spectra of the acceptor and PTB7-Th, respectively. In other words, the absorption spectra of the small molecule acceptor and PTB7-Th donor contributed to the photocurrent of PTB7-Th:acceptor devices. Moreover, the EQE responses of the devices increased upon annealing (TA or SVA treatment), as expected based on the higher J_{SC} values

Small molecule	Annealing	$V_{\rm OC}$ (V)	$J_{\rm SC}~({\rm mA/cm}^2)$	FF (%)	PCE (%)
TT-BBAR	w/o	0.61	1.94	56	0.67
	TA^b	0.80	2.06	44	0.72
	SVA^{c}	0.87	2.97	45	1.16
TT-OBAR	w/o	0.72	3.11	50	1.12
	TA^b	0.89	3.59	42	1.34
	SVA^{c}	0.90	3.43	42	1.29

^a Open circuit voltage (V_{OC}), short-circuit current (J_{SC}), and fill factor (FF).

^b TA at 90 °C.

^c SVA using THF.

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Figure 4. AFM height images of the (a) PTB7-Th:**TT-BBAR** and (b) PTB7-Th:**TT-OBAR** blend films $(2 \times 2 \ \mu m)$.

obtained after annealing. For example, the EQE maxima of the PTB7-Th:**TT-OBAR** devices increased from 20 to 23% by SVA treatment. In addition, the introduction of the third component having complementary UV–Vis absorption spectra could further improve device performances.

AFM images were obtained to characterize the film morphologies and are shown in Figures 4 and S4. The PTB7-Th:**TT-BBAR** blend film displayed a rougher surface with a root-mean-square (RMS) roughness of 11.7 nm, whereas the blend film prepared using PTB7-Th:**TT-OBAR** had very smooth surface with a RMS of 1.18 nm. **TT-OBAR** formed a more homogeneous film compared to **TT-BBAR**. In other words, the longer alkyl chain of **TT-OBAR** may have improved the small molecule solubility and morphology, thereby providing better J_{SC} and PCE values for the PTB7-Th:**TT-OBAR** blend film.

Conclusion

We synthesized two non-fullerene small molecule acceptors, **TT-BBAR**, and **TT-OBAR**, containing alkylsubstituted BAR end groups. They have sufficient solubility and thermal stability for application in OPV devices. The electrochemical and optical properties of **TT-BBAR** and **TT-OBAR** were found be similar, regardless of the alkyl chain length; however, a smoother and more homogeneous film morphology was obtained from the **TT-OBAR**-based blend film, due to the longer alkyl chain and the better solubility of **TT-OBAR**. The PTB7-Th:**TT-OBAR** device exhibited a better PCE of 1.34% together with a high J_{SC} value of 3.59 mA/cm².

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Supporting Information. Additional supporting information may be found online in the Supporting Information section at the end of the article.

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