Facile Synthesis of *o*-Xylenyl Fullerene Multi-adducts for High Open Circuit Voltage and Efficient Polymer Solar Cells

Supporting Information

Ki-Hyun Kim,[a] Hyunbum Kang,[a] So Yeon Nam,[b] Jaewook Jung,[b] Pan Seok Kim,[b] Chul-Hee Cho,[a] Changjin Lee,[b] Sung Cheol Yoon*[b] and Bumjoon J. Kim*[a]

[a] *Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Korea*

[b] *Advanced Materials Division, Korea Research Institute of Chemical Technology (KRICT), Daejeon 305-600, Korea*

1. Materials and Methods

All commercially available reagents were used without further purification. The organic solvents were used as anhydrous solvents. Analytical thin-layer chromatography (TLC) was performed using Merck silica gel 60 F254 precoated plates (0.25 mm) with a fluorescent indicator and visualized with UV light

(254 and 365 nm). Flash column chromatography was carried out on Merck silica gel 60 (230-400 mesh). All ^{1}H-NMR spectra were recorded at 500 MHz, using $CDCl_3$ as a solvent, unless otherwise stated. The chemical shifts of all ^{1}H-NMR spectra are referenced to the residual signal of $CDCl_3$ (δ 7.26 ppm) by Bruker 500 MHz NMR instrument. All coupling constants, *J*, are reported in Hertz (Hz). MALDI-TOF mass spectra were recorded on a Bruker autoflex III mass spectrometer. Elemental analysis was performed with a ThermoQuest Italia S.P.A model EA1110-FISONS. UV-visible absorption spectra were obtained using a Shimadzu UV-Vis-NIR 3600 spectrophotometer. Cyclic voltammetry (CV) curves were measured using a CHI 600C electrochemical analyzer. Cyclic voltammogram of the different electron acceptors were collected at room temperature using a conventional three-electrode system (Pt disk working electrode, Pt wire counter-electrode and Ag wire quasi-reference electrode) in 0.1 M tetrabutylammonium tetrafluoroborate (NBu_4BF_4) solution in *o*-dichlorobenzene at a potential scan rate of 10 mV/s. The reduction potentials of the acceptor solutions against the Ag quasi-reference electrode were measured and calibrated against a ferrocene/ferrocenium (Fc/Fc^+) redox couple, assuming that the absolute energy level of Fc/Fc^+ was -4.80 eV.[1,2,3]

2. Detail experimental procedures

General procedure for preparation of o-xylenyl C_{60} multi-adducts

Mixture of C_{60} (1 equiv), α,α'-dibromo-*o*-xylene (1 equiv; for OXCMA, 2 equiv; for OXCBA, and 3 equiv; for OXCTA), potassium iodide (4 equiv to α,α'-dibromo-*o*-xylene), and 18-crown-6 (1 equiv to potassium iodide) were dissolved in anhydrous *o*-dichlorobenzene at reflux temperature for 48 h under an argon atmosphere in dark. After cooling to room temperature, the reaction mixture were adsorbed on

silica gel, and then purified by using flash silica column chromatography (Merck silica gel 60, 230-400 mesh) with hexane/toluene (v/v) as the gradient eluents (1/0 for unreacted C_{60}, 10/1 for OXCMA, 8/1 for OXCBA, 6/1 for OXCTA). Then, desired product was concentrated *in vacuo* and precipitated in excess MeOH to give brown solid.

OXCMA. When 400 mg of C_{60} was reacted with 144 mg of *α*,*α*'-dibromo-*o*-xylene, the crude products consisted of OXCMA as the main product, a very small amount of OXCBA, and unreacted fullerene. The amounts of isolated OXCMA was 120 mg with 26% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.69-7.67 (m, 2H), 7.57-7.55 (m, 2H), 4.83 (d, J = 11.2, 2H), 4.44 (d, J = 12.4, 2H); elemental analysis for $C_{68}H_8$: calculated: C, 99.02; H, 0.98; found: C, 97.17; H, 1.36. MALDI-TOF MS: calculated for $C_{69}H_8$ 824.06; found: 824.86 (M^+).

OXCBA. When 1 g of C_{60} was reacted with 725 mg of *α*,*α*'-dibromo-*o*-xylene, the crude products consisted of OXCBA as the main product, a small amount of OXCMA, and OXCTA. The amounts of isolated OXCBA was 540 mg with 42% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.90-7.14 (m, 8H), 5.03-3.37 (m, 8H); elemental analysis for $C_{76}H_{16}$: calculated: C, 98.26; H, 1.74; found: C, 97.52; H, 1.99. MALDI-TOF MS: calculated for $C_{69}H_8$ 928.13; found: 928.45 (M^+).

OXCTA. When 1 g of C_{60} was reacted with 1.17 g of *α*,*α*'-dibromo-*o*-xylene, the crude products consisted of OXCTA as the main product, and a small amount of OXCBA, The amounts of isolated OXCTA was 430 mg with 30% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.75-7.10 (m, 12H), 4.75-3.25 (m,

12H); elemental analysis for $C_{84}H_{24}$: calculated: C, 97.66; H, 2.34; found: C, 96.25; H, 2.45. MALDI-TOF MS: calculated for $C_{69}H_8$ 1032.19; found: 1032.57 (M^+).

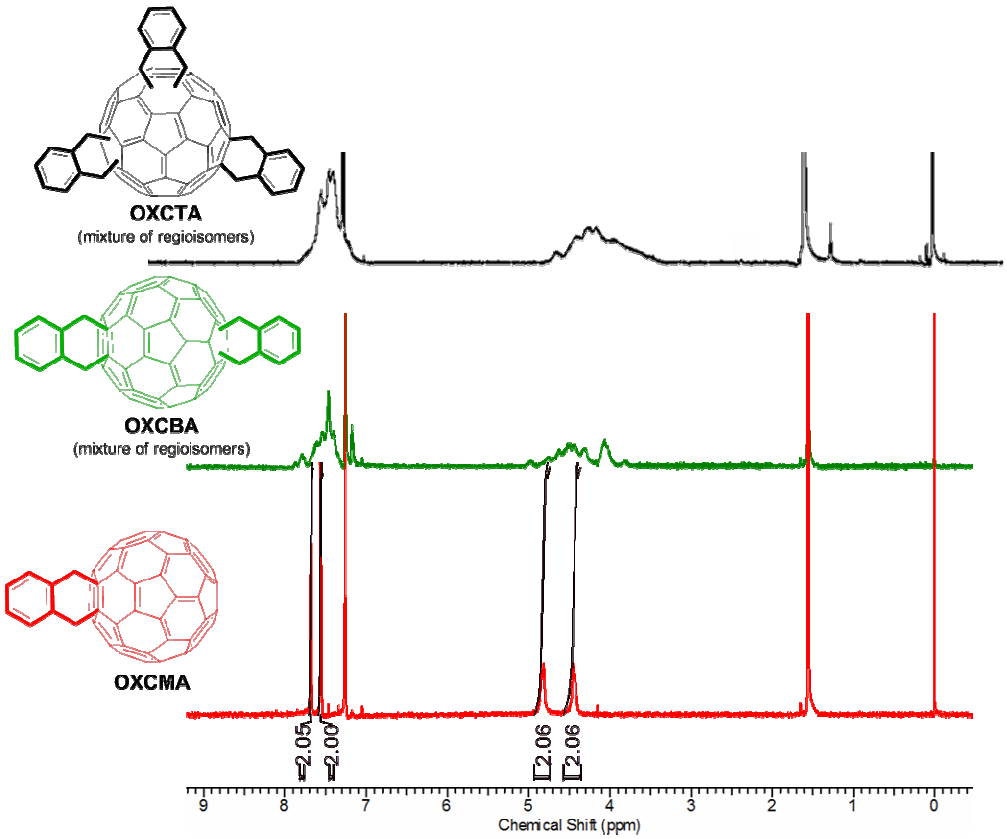

Figure S1. ^{1}H-NMR data of OXCMA, OXCBA, and OXCTA.

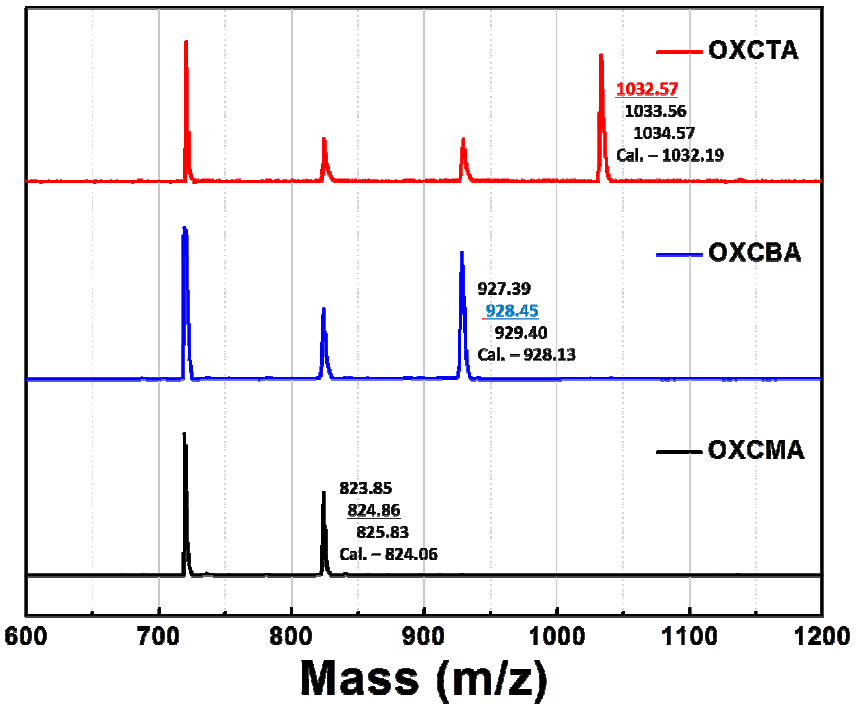

Figure S2. MALDI-TOF data of OXCMA, OXCBA, and OXCTA.

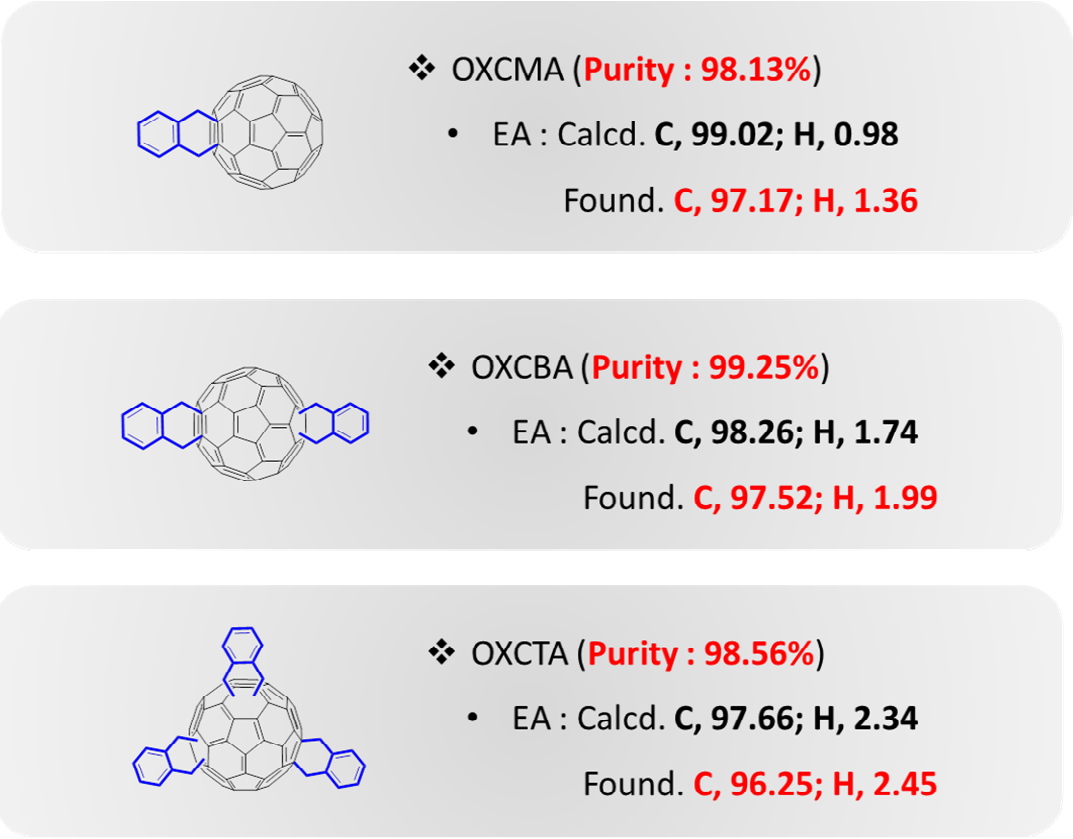

Figure S3. EA data of OXCMA, OXCBA, and OXCTA.

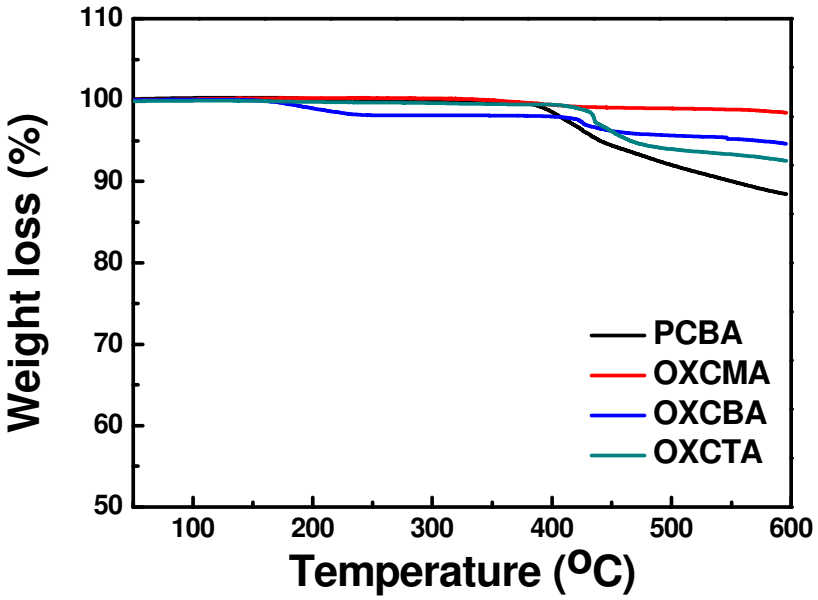

Figure S4. TGA data of PCBM, OXCMA, OXCBA, and OXCTA.

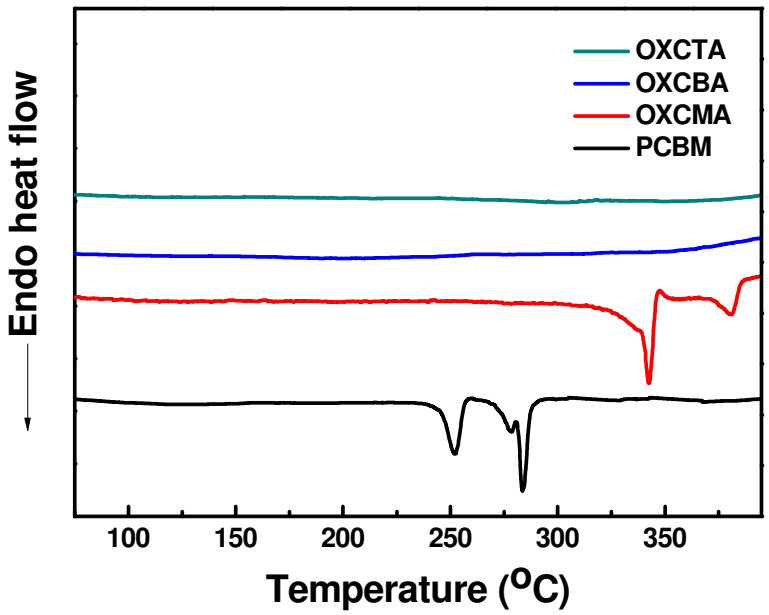

Figure S5. DSC data of PCBM, OXCMA, OXCBA, and OXCTA.

Solar Cell Fabrication

To investigate the photovoltaic properties of the *o*-xylenyl C_{60} multi-adducts, BHJ photovoltaic cells using an ITO/PEDOT:PSS/P3HT:Electron acceptor/LiF/Al structure were fabricated; P3HT (BASF P200) was used as an electron donor, and PCBM, OXCMA, OXCBA, and OXCTA were used as electron acceptors. ITO-coated glass substrates were subjected to ultrasonication in acetone and 2% Helmanex soap in water, followed by extensive rinsing with deionized water and ultrasonication in deionized water and then in isopropyl alcohol; the substrates were finally dried for several hours in an oven at 80 ˚C. A filtered dispersion of PEDOT:PSS in water (BAYTRON AI 4083) was applied by spin-coating at 2,000 rpm for 40 sec and baking for 20 min at 150 °C in air. A thickness of PEDOT:PSS film was about ~40 nm. After application of the PEDOT:PSS layer, all subsequent procedures were performed in a glove box under a N_2 atmosphere. Solutions of P3HT and PCBM, OXCMA, OXCBA, and OXCTA were prepared in *o*-dichlorobenzene and stirred at 100 °C overnight to ensure complete dissolution. Immediately prior to solution deposition, the solutions were passed through a 0.2-μm polytetrafluoroethylene syringe filter. For the P3HT devices using PCBM, OXCMA, OXCBA, and OXCTA the blend solution was stirred at RT for 1 h and then spun-cast onto the ITO/PEDOT:PSS substrates at 900 rpm. Each P3HT/acceptor film was placed in air in order to completely dry the film and thickness of films was about ~120 nm. The substrates were then placed in an evaporation chamber and held under high vacuum (less than 10^{-6} Torr) for more than 1 h before evaporating approximately 0.5 nm of LiF/ 150 nm of Al. The configuration of the shadow mask afforded four independent devices on each substrate. After encapsulating the active layer using an encap glass, thermal annealing was performed for 10 min at 150 °C to optimize the morphology of the BHJ active layer and improve the device performance by promoting polymer self-organization. The photovoltaic performances were characterized using a solar simulator (Newport Oriel Solar Simulators) with an air-mass (AM) 1.5 G filters. The intensity of the solar simulator was carefully calibrated using an AIST-certified silicon photodiode. Current-voltage behavior was measured using a Keithly 2400 SMU. The active area of the fabricated devices was 0.09 cm^2.

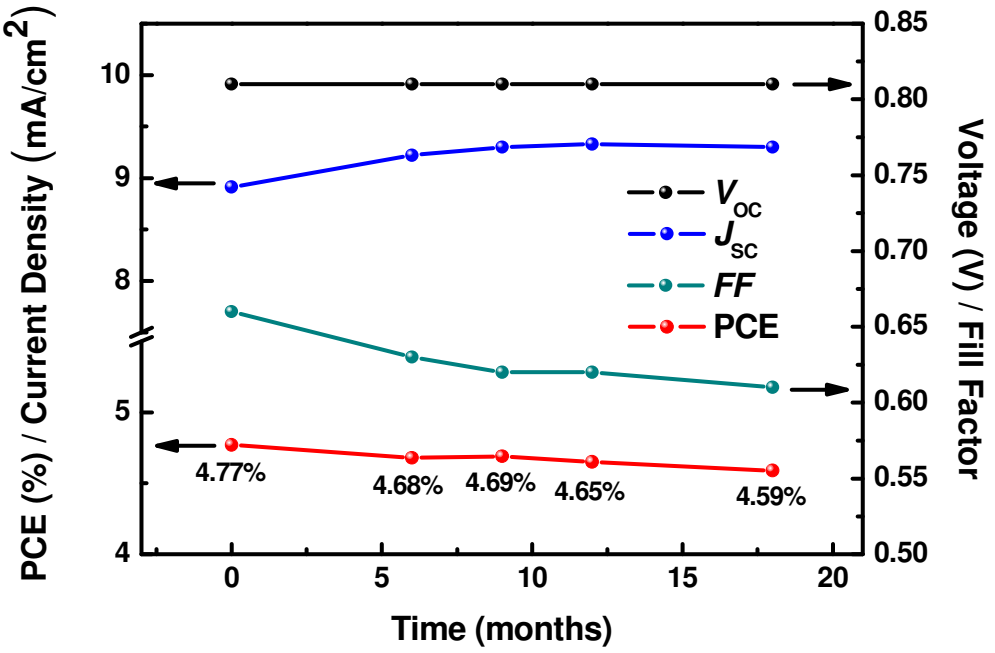

Figure S6. Variation of of V_{OC} (black line), J_{SC} (blue line), *FF* (green line), and PCE (red line) of P3HT:OXCBA (1:0.7) devices as a function of the number of months after fabrication.

Table S1. Performance variation of P3HT:OXCBA (1:0.7) based polymer solar cells as a function of the number of months after fabrication

Shelf Lifetime (months)	V_{OC} (V)	J_{SC} (mA·cm^{-2})	*FF*	PCE (%)
0	0.81	8.91	0.66	4.77
6	0.81	9.22	0.63	4.68
9	0.81	9.30	0.62	4.69
12	0.81	9.33	0.62	4.65
18	0.81	9.30	0.61	4.59

Space-charge-limited current method

Hole mobilities of the P3HT used as an electron donor in the blended system were measured by the space-charge-limited current (SCLC) method using the device structure of ITO/PEDOT:PSS/blend/Au; current-voltage measurements in the range of 0–8 V were taken, and the results were fitted to a space-charge-limited form. The SCLC is described by:

$$J_{SCLC} = \frac{9}{8}\varepsilon\varepsilon_0\mu\frac{V^2}{L^3}$$

where ε_0 is the permittivity of free space, ε is the dielectric constant of the polymer, μ is the mobility of the charge carriers, V is the potential across the device ($V = V_{applied}-V_{bi}-V_r$), and L is the polymer layer thickness. The series and contact resistance of the device (~25 Ω) was measured using a blank device (ITO/PEDOT/Au), and the voltage drop due to this resistance (V_r) was subtracted from the applied voltage. Electron-only devices with the structure ITO/CS_2CO_3/blend/LiF/Al were also fabricated by spin-coating the active layer on ITO/CS_2CO_3 substrates followed by the deposition of LiF/Al on the cathode electrode, as reported in the literature.[3]

Reference

(1) Liang, Y.; Feng, D.; Wu, Y.; Tsai, S.-T.; Li, G.; Ray, C.; Yu, L. *Journal of the American Chemical Society* 2009, *131*, 7792.
(2) Chang, Y.-T.; Hsu, S.-L.; Chen, G.-Y.; Su, M.-H.; Singh, T. A.; Diau, E. W.-G.; Wei, K.-H. *Adv Funct Mater* 2008, *18*, 2356.
(3) Lee, J. M.; Park, J. S.; Lee, S. H.; Kim, H.; Yoo, S.; Kim, S. O. *Adv Mater* 2011, *23*, 629.