

Electronic Supplementary Information

Dumb-belled PCBM derivative with better photovoltaic performance

Juan Liu, Xia Guo, Yujun Qin, Shengde Liang, Zhi-Xin Guo and Yongfang Li

Experimental details

Materials. C60 was purchased from Yongxin Co. (China). 1-ethyl-3-(3-(dimethylamino) propyl) carbodiimide (EDC), 4-(dimethylamino) pyridine (DMAP), neopentyl alcohol, 2, 2-dimethyl-1,3-propanediol and 2-(hydroxymethyl)-2-methylpropane-1,3-diol were purchased from Alfa-Aesar Co. P3HT was purchased from Rieke Metals and used as received. Other materials were commercially available.

Measurements. ^1H and ^{13}C NMR were measured on a Bruker DMX-400 spectrometer. Chemical shift were reported in ppm relative to the singlets of CDCl_3 at 7.28 and 77 ppm for ^1H and ^{13}C NMR, respectively. Absorption spectra were recorded with a Varian Cary 50 UV-vis spectrophotometer. Electrochemical cyclic voltammetry was conducted on Epsilon/100BWBAS electrochemical workstation with glassy carbon electrode, Pt wire, and Ag/Ag^+ electrode as working electrode, counter electrode, and reference electrode, respectively in a 0.1 M Bu_4NClO_4 , dichlorobenzene/acetonitrile (5:1, v/v) solution. The surface morphologies of the P3HT/fullerene derivatives blend films (1:1, w/w) were characterized by atomic force microscopy (AFM; instrument: Dimensional 3100, Veeco Co.).

Syntheses of Fullerene Derivatives. PCBM and [6, 6]-phenyl- C_{61} -butyric acid (PCBA) was synthesized according to the literature.¹ The chemical structures of PCBM and other fullerene derivatives studied in the paper are shown in Scheme 1 and their syntheses are as follows.

MP: EDC (94.9 mg, 0.5 mmol) was added portionwisely to a pre-cooled suspension of neopentyl alcohol (13.2 mg, 1.65 mmol), PCBA (30.0 mg, 0.33 mmol), and some DMAP in 20 mL dry dichloromethane. The mixture was stirred overnight in room temperature.² After evaporation of the solvent under reduced pressure the residue was purified by column chromatography (silica gel, toluene). The obtained product was further precipitated from methanol affording pure MP as a dark-brown solid. Yield: 59.0%. ^1H NMR(CDCl_3 , 400MHz) (Fig. 1s): δ 0.94 (9H, s), 2.23 (2H, m, $J=5.22$ Hz), 2.57 (2H, t, $J=7.44$ Hz), 2.94 (2H, m, $J=4.10$ Hz), 3.80 (2H, s), 7.49 (1H, t, $J=7.34$ Hz), 7.57 (2H, t, $J=7.44$ Hz), 7.95 (2H, d, $J=7.24$ Hz); ^{13}C NMR(CDCl_3 , 400MHz) (Fig. 2s): 22.51 ($\text{PhCCH}_2\text{CH}_2$), 26.50 (CH_3), 31.29 ($\text{C}(\text{CH}_3)_3$), 33.76, 34.20 ($\text{CH}_2\text{CO}_2\text{CH}_2\text{C}(\text{CH}_3)_3$ and PhCCH_2), 51.95 (PhCCH_2), 73.87 (OCH_2),

79.95(bridgehead C), 128.24(PhC_{2,3}), 128.43(PhC₄), 132.12, 136.78, 137.59, 138.09, 140.76, 141.02, 142.21, 143.05, 143.79, 144.03, 144.45, 144.53, 144.69, 144.81, 145.08, 145.19, 145.88, 147.83, 148.85, 173.09(CO₂CH₂C(CH₃)₃). MALDI-TOF-MS m/z: calcd for 966.2, found 966.5.

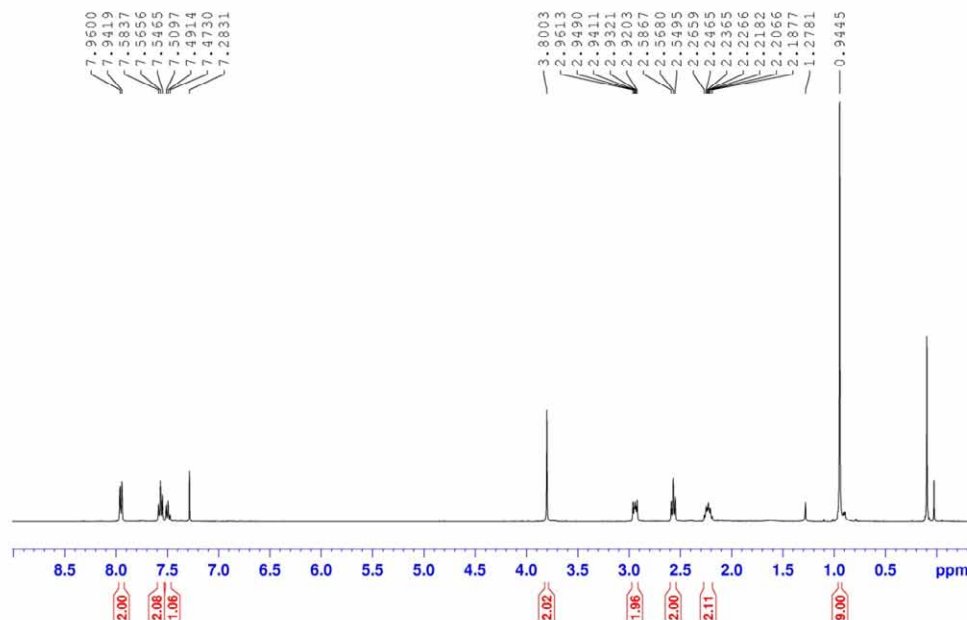


Fig. 1s ¹H NMR spectrum of MP.

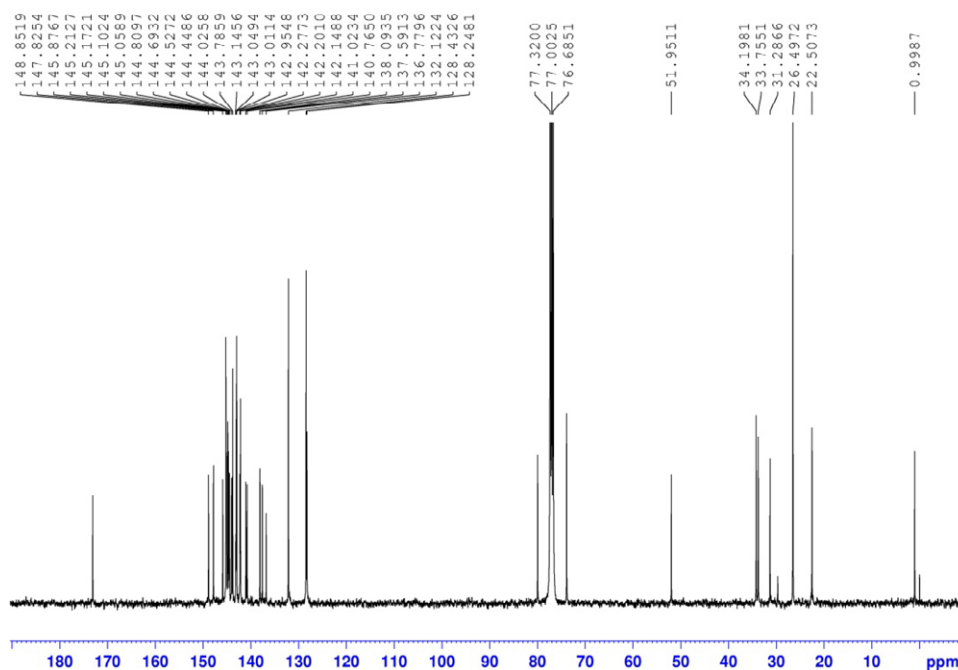


Fig. 2s ¹³C NMR spectrum of MP.

BP: Compound BP was prepared by the same method as that for the synthesis of compound MP, except 2, 2-dimethyl-1, 3-propanediol was used instead of neopentyl alcohol. Yield: 35.5%. ¹H NMR (CDCl₃, 400Hz) (Fig. 3s): δ 0.95 (6H, s),

2.21 (4H, q, $J=5.19$ Hz), 2.55 (4H, s), 2.93 (4H, q, $J=5.44$ Hz), 3.90 (4H, s), 7.49 (2H, t, $J=7.30$ Hz), 7.56 (4H, t, $J=7.40$ Hz), 7.95 (4H, d, $J=7.24$ Hz). ^{13}C NMR (CDCl_3 , 400Hz) (Fig. 4s): 21.83 (CH_3), 22.42 ($\text{PhCCH}_2\text{CH}_2$), 33.70, 34.03 ($\text{CH}_2\text{CO}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CO}_2\text{CH}_2$ and PhCCH_2), 34.72 ($\text{C}(\text{CH}_3)_2$), 51.87 (PhCCH_2), 69.33 ($\text{OCH}_2\text{C}(\text{CH}_3)_2\text{OCH}_2$), 79.91 (bridgehead C), 128.21, 128.46, ($\text{PhC}_{2,3}$, PhC_4), 132.12, 136.75, 137.60, 138.07, 140.78, 141.02, 142.21, 143.06, 143.78, 144.03, 144.49, 144.75, 145.15, 145.88, 147.80, 148.80, 172.80 ($\text{CO}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{CO}_2$). MALDI-TOF-MS m/z : calcd for 1861.2, found 1861.7.

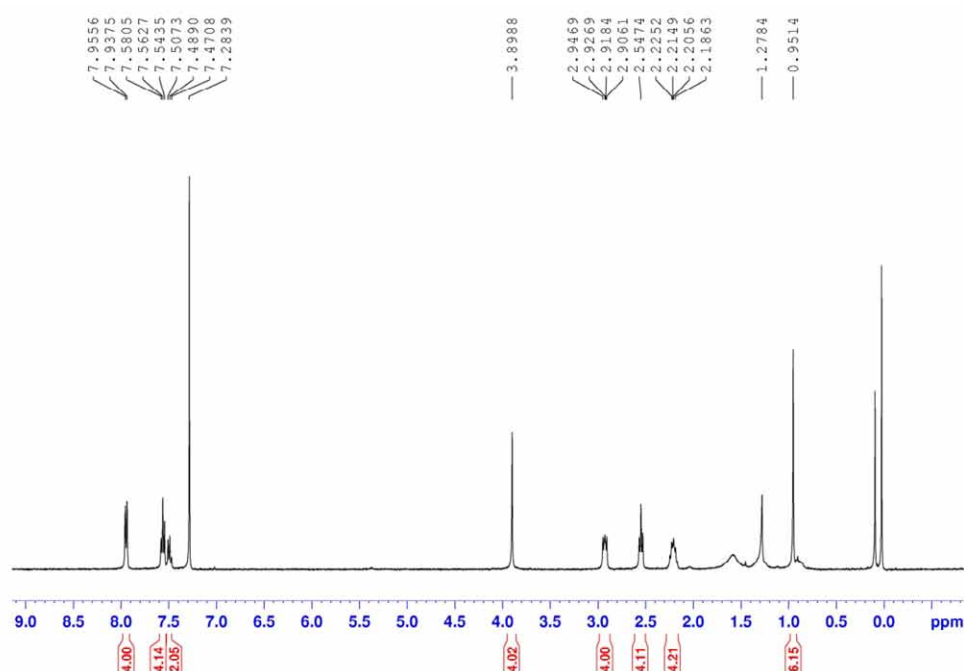


Fig. 3s ^1H NMR spectrum of DP.

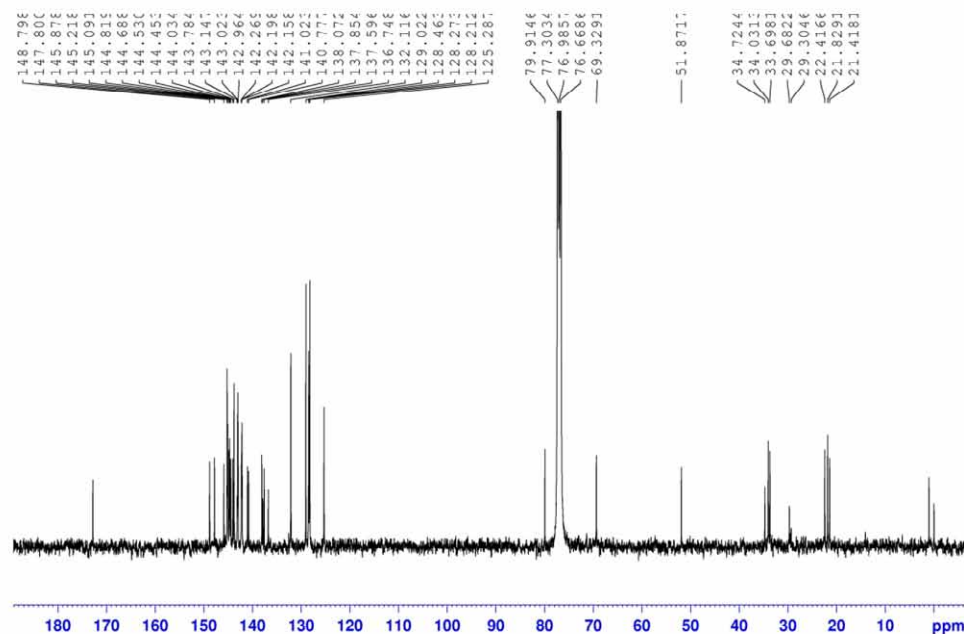


Fig. 4s ^{13}C NMR spectrum of DP.

TP: Compound TP was prepared by the same method as that for the synthesis of compound MP, except 2-(hydroxymethyl)-2-methylpropane-1, 3-diol was used instead of neopentyl alcohol. Yield: 36.0%. ^1H NMR ($\text{CS}_2/\text{CDCl}_3$, 400Hz) (Fig. 5s): δ 0.98(3H, s), 2.20 (6H, t, $J=7.32$ Hz), 2.53 (6H, t, $J=7.10$ Hz), 2.92 (6H, t, $J=7.90$ Hz), 4.00 (6H, s), 7.48 (3H, t, $J=7.14$ Hz), 7.55 (6H, t, $J=7.32$ Hz), 7.94 (6H, d, $J=7.36$ Hz). ^{13}C NMR ($\text{CS}_2/\text{CDCl}_3$, 400Hz) (Fig. 6s): 17.23 (CH_3), 22.51 ($\text{PhCCH}_2\text{CH}_2$), 33.76, 33.93(CH_2CO_2 and PhCCH_2), 38.49 ($\text{C}(\text{CH}_2\text{CO}_2)_2\text{CH}_3$), 51.81 (PhCCH_2), 65.84 (OCH_2), 79.84 (bridgehead C), 128.33, 128.58 ($\text{PhC}_{2,3}$, PhC_4), 132.12, 136.69, 137.71, 138.10, 140.85, 141.08, 142.22, 143.05, 143.82, 144.13, 144.54, 144.79, 145.19, 145.88, 147.72, 148.65, 172.12 ($\text{CO}_2\text{CH}_2\text{C}(\text{CH}_2\text{CO}_2)_2\text{CH}_3$). MALDI-TOF-MS m/z : calcd for 2756.3, found 2756.4.

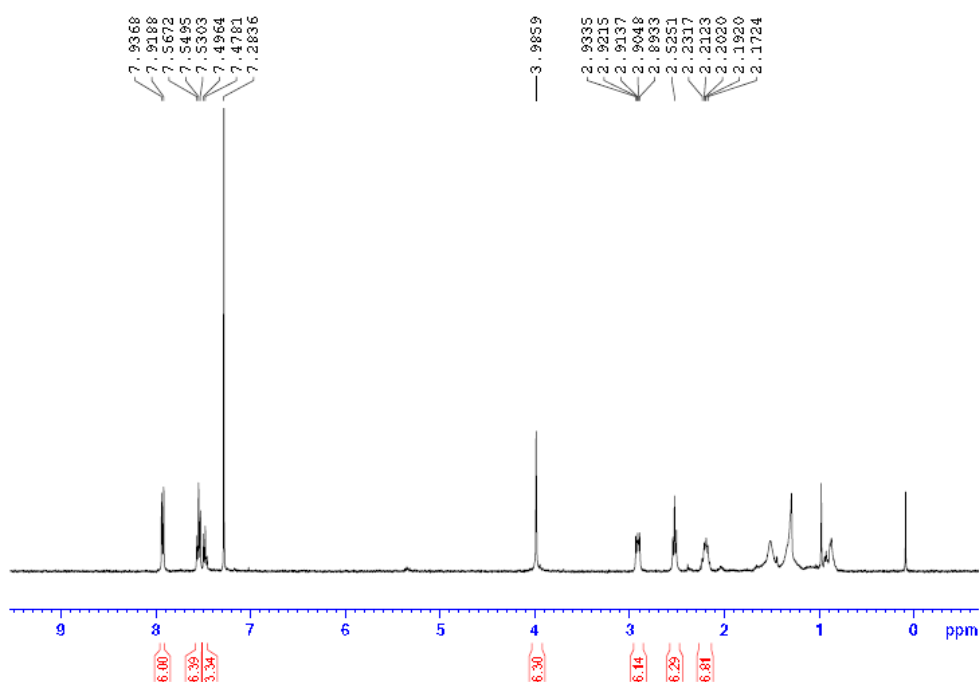


Fig. 5s ^1H NMR spectrum of TP.

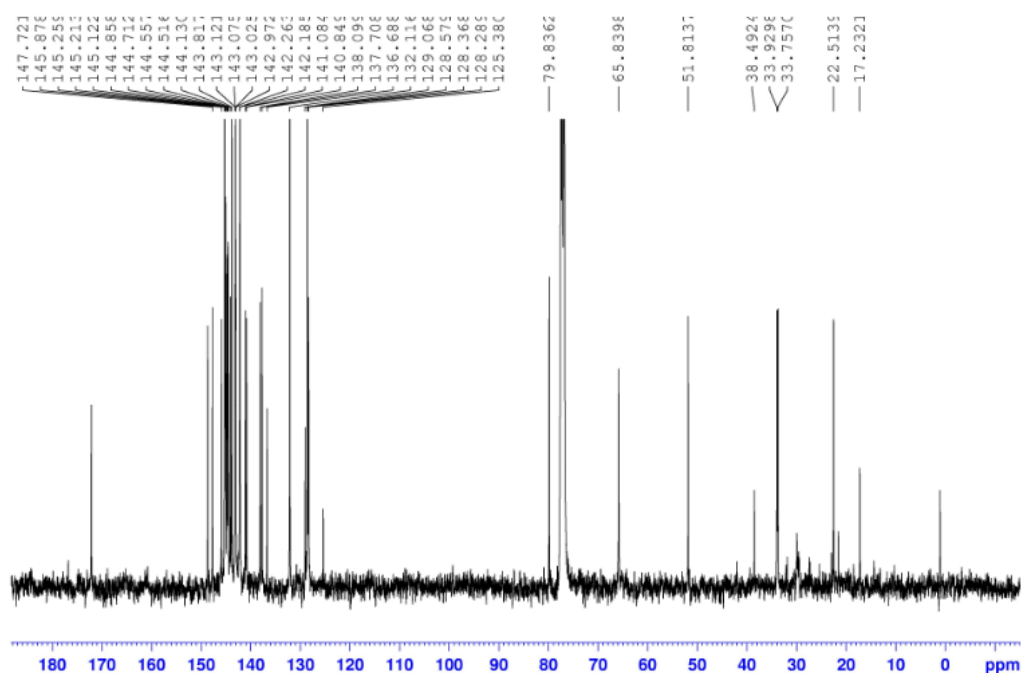


Fig. 6s ^{13}C NMR spectrum of MP.

Fabrication and Characterization of PSCs. The PSCs were fabricated in the configuration of the traditional sandwich structure with an indium tin oxide (ITO) glass positive electrode and a metal negative electrode.³⁻⁵ Patterned ITO glass with a sheet resistance of $10 \Omega \text{ sq}^{-1}$ was purchased from CSG Holding Co., Ltd. (China). The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water,

acetone, and isopropanol, and then treated in an ultraviolet-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 15 min. Then PEDOT:PSS (poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate)) (Clevios P VP AI 4083 H. C. Stark, Germany) was filtered through a 0.45 μm filter and spin coated at 4000 rpm for 60 s on the ITO electrode. Then, the PEDOT: PSS film was baked at 150 $^{\circ}\text{C}$ for 10 min in the air. The P3HT and acceptors (1:1 wt ratio, 1:1 wt ratio, 17 mg/mL for each) were dissolved in *o*-dichlorobenzene separately to make a blend solution. The solution was spin-coated on top of the PEDOT:PSS layer of ITO at 800 rpm for 30s. The active layers were optimized by solvent annealing for 2 h and pre-thermal annealing at 150 $^{\circ}\text{C}$ for 10 min. Then, the negative electrode consisted of Ca (~ 20 nm) capped with Al (~ 100 nm) was thermally evaporated on the active layer under a shadow mask in a base pressure of ca. 10^{-4} Pa. The device active area is ~ 4 mm^2 for all the PSCs discussed in this work. Twenty cells were prepared for each study carried out with the compounds.

The current density-voltage (*I-V*) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. Device characterization was done in glove box under the illumination of AM1.5G, 100 mW cm^{-2} , using a 150 W xenon-lamp-based solar simulator (from Newport Co., Ltd.). The reference cell is a Schott visible-color glass-filtered (KG5 color filtered) Si diode (Hamamatsu S1133). The external quantum efficiency (EQE) was measured by Stanford Research Systems model SR830 DSP lock-in amplifier coupled with WDG3 monochromator and 500 W xenon lamp. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

References

1. J. C. Hummelen, B. W. Knight, F. Lepeq, F. Wudl, J. Yao and C. L. Wilkins, *J. Org. Chem.*, 1995, **60**, 532-538.
2. F. Giacalone, J. L. Segura and N. Martin, *J. Org. Chem.*, 2002, **67**, 3529-3532.
3. G. Li, V. Shrotriya, J. S. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nat. Mater.*, 2005, **4**, 864-868.
4. Y. He, H.-Y. Chen, J. Hou and Y. Li, *J. Am. Chem. Soc.*, 2010, **132**, 1377-1382.
5. G. J. Zhao, Y. J. He and Y. F. Li, *Adv. Mater.*, 2010, **22**, 4355-4358.