Supporting Information

Thermo-cleavable fullerene materials as a buffer layer for efficient polymer solar cells

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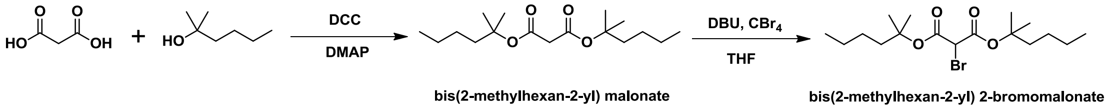
1. General characterization

NMR spectra were measured on a Bruker AVANCE-400 spectrometer. Mass spectra were measured on a Bruker Apex IV FIMS spectrometer. UV-Vis absorption spectra were recorded on a SHIMADZU UV-1800 spectrophotometer. IR spectra were measured by a Nicolet Magna 750 FTIR Spectrometer. Cyclic voltammetry (CV) was performed using a SHANGHAI CHENHUA CHI620D voltammetric analyzer. CV measurements were carried out in a cell under Ar gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and a Ag/Ag$^+$ reference electrode. Measurements were performed in ODCB/CH_3CN (9:1) solution containing tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) as a supporting electrolyte with a scanning rate of 0.1 V/s. All potentials were corrected against Fc/Fc$^+$. Thermogravimetric analysis (TGA) was carried out by a PerkinElmer

Diamond TG/DTA thermal analyzer. AFM characterization was carried out on a Dimension ICON microscope (Bruker) (tapping mode). Contact angle measurements were performed using a Kaüss DSA-100 instrument.

2. Synthetic procedures and spectra data

P3HT was purchased from Rieke Metals Inc. PBDTTT-C was purchased from Solarmer Materials Inc. C_{60} and C_{70} were purchased from YongXin Co. (China). Reagents and chemicals were purchased from Alfa-Aesar Co., TCI Co., or other commercial suppliers and used as received. $PC_{61}BM$, $PC_{71}BM$, and $CHBr(COO^{t}Bu)_2$ were synthesized according to literature.[1-3]



Scheme S1 Synthetic route for bis(2-methylhexan-2-yl) 2-bromomalonate.

Synthesis of bis(2-methylhexan-2-yl) malonate

Malonic acid (2 g, 19.2 mmol), 2-methylhexan-2-ol (4.46 g, 38.4 mmol), N,N'-Dicyclohexylcarbodiimide (DCC) (7.96 g, 38.4 mmol) and 4-Dimethylaminopyridine (DMAP) (60 mg,) were added into toluene (40 mL), and stirred at room temperature for 3 h (Scheme S1). Then, toluene was removed by vacuum rotary evaporation. The residue was purified by silica gel column chromatography (petroleum ether/chloroform(1:1) as the eluent) and afforded bis(2-methylhexan-2-yl) malonate (1.52 g, yield: 26%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 3.19 (s, 2H), 1.78-1.70 (m, 4H), 1.45 (s, 12H), 1.30 (m, 8H), 0.90 (t, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 14.82, 23.77, 26.64, 26.81, 41.38, 45.22, 84.77, 166.83.

Synthesis of bis(2-methylhexan-2-yl) 2-bromomalonate

Bis(2-methylhexan-2-yl) malonate (520 mg, 1.73 mmol) was dissolved in THF (100 mL) at 0 °C. DBU (260 μL, 1 mmol) was added at 0 °C. The reaction was warmed up to room temperature for 1 h, then cooled to -78 °C and CBr_4 (575 mg, 1.73 mmol) was added (Scheme S1). The mixture was stirred for 3 h at -78 °C and quenched with saturated aqueous solution of NH_4Cl. The phases were separated and hexane was added to the organic phase. The organic part was washed twice with brine. The aqueous part was extracted twice with CH_2Cl_2. The organic parts were combined, dried over anhydrous magnesium sulfate and concentrated by vacuum rotary evaporation. The residue was purified by silica gel column chromatography (diethyl ether/n-hexane(1:4) as the eluent) and afforded bis(2-methylhexan-2-yl) 2-bromomalonate (220 mg, yield: 34%). ^{1}H NMR ($CDCl_3$, 400 MHz,) δ (ppm): 4.66 (s, 1H), 1.79 -1.74 (m, 4H), 1.47 (s, 12H), 1.31 (m, 8H), 0.91 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 14.79, 23.72, 26.31, 26.46, 26.70, 41.27, 46.52, 87.08, 164.30.

3. NMR spectra

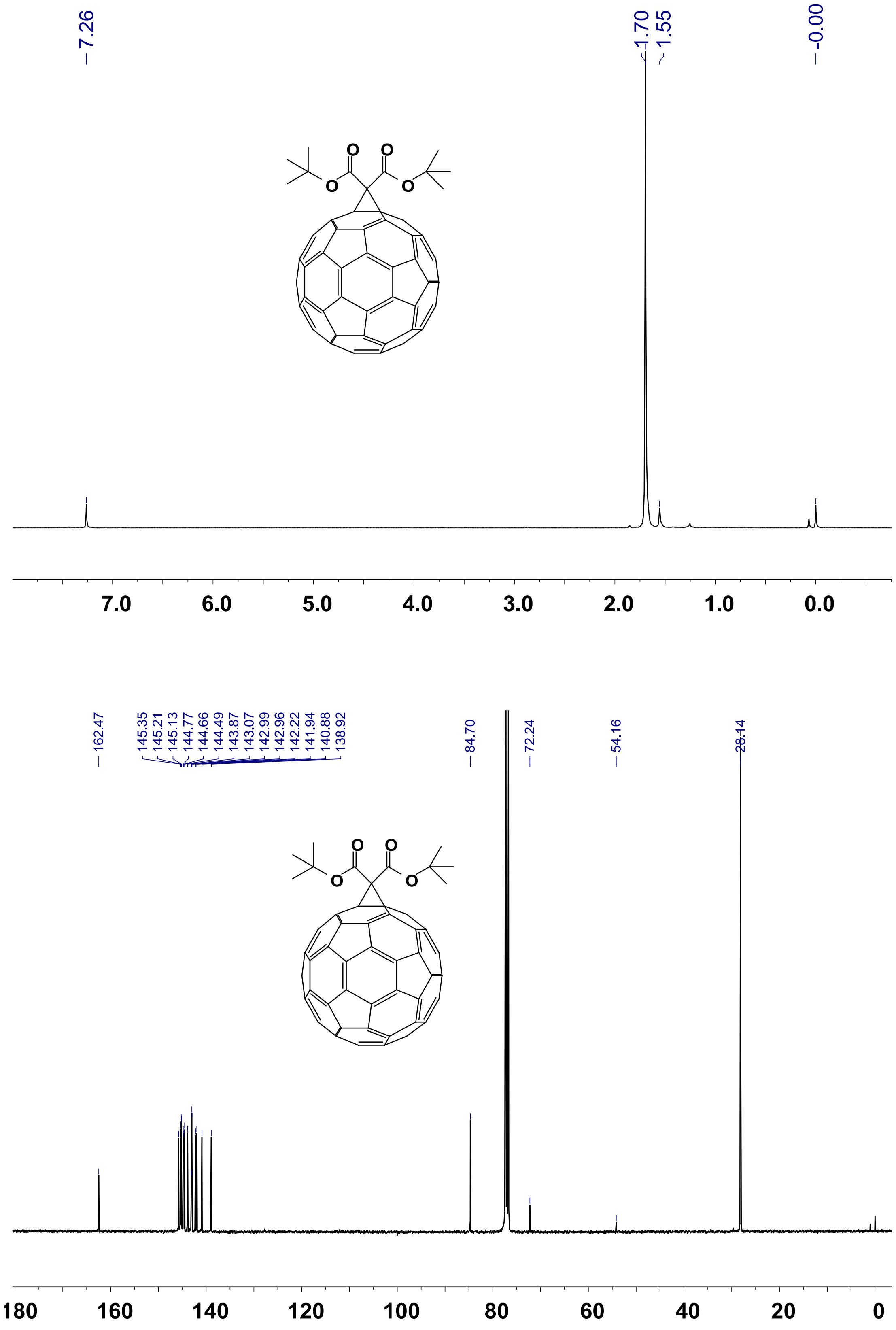


Fig. S1 ^{1}H NMR (in $CDCl_3$, top) and ^{13}C NMR (in $CDCl_3/CS_2$, bottom) of DBMD.

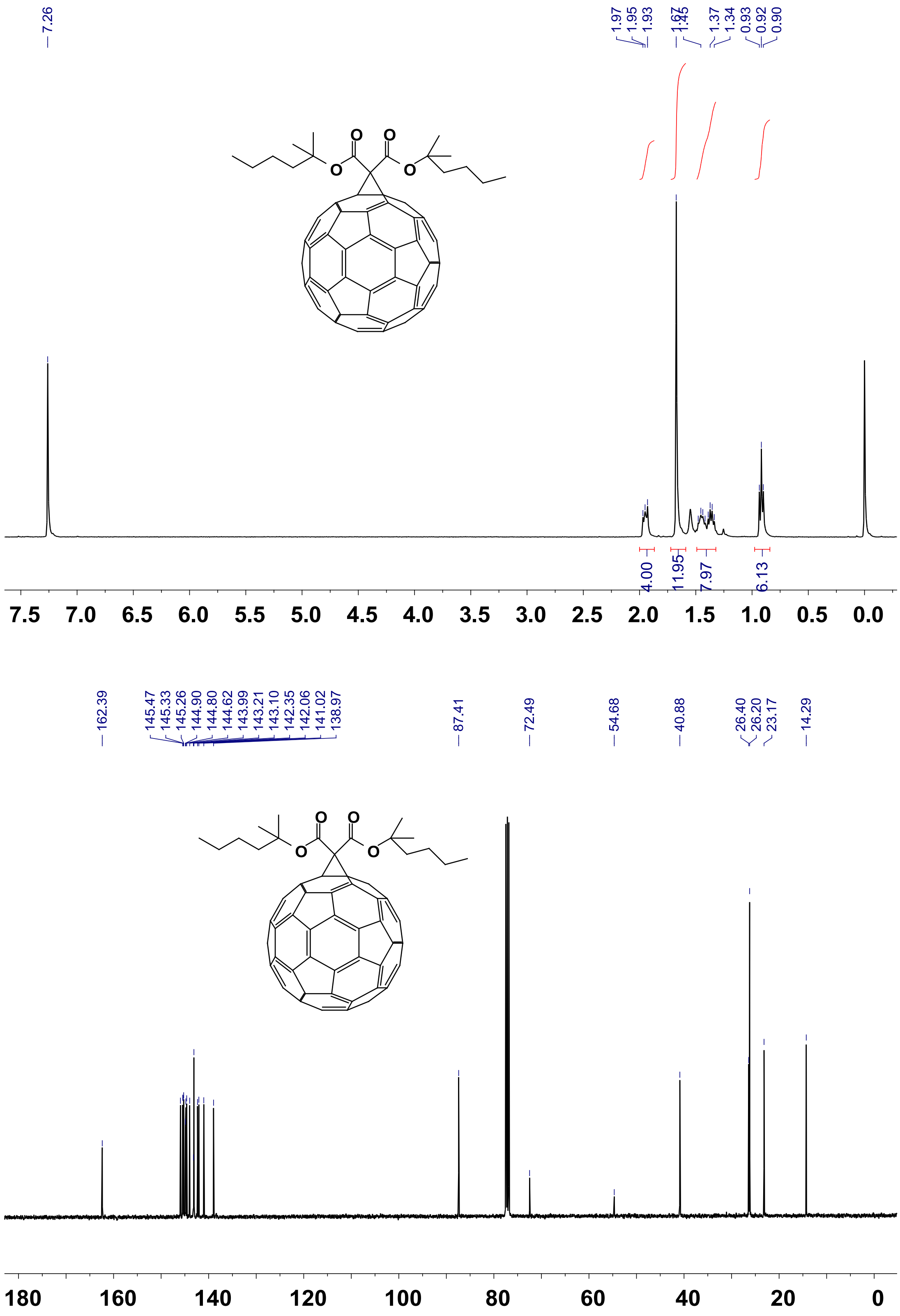


Fig. S2 ^{1}H NMR (in $CDCl_3$, top) and ^{13}C NMR (in $CDCl_3$, bottom) of BMHMD.

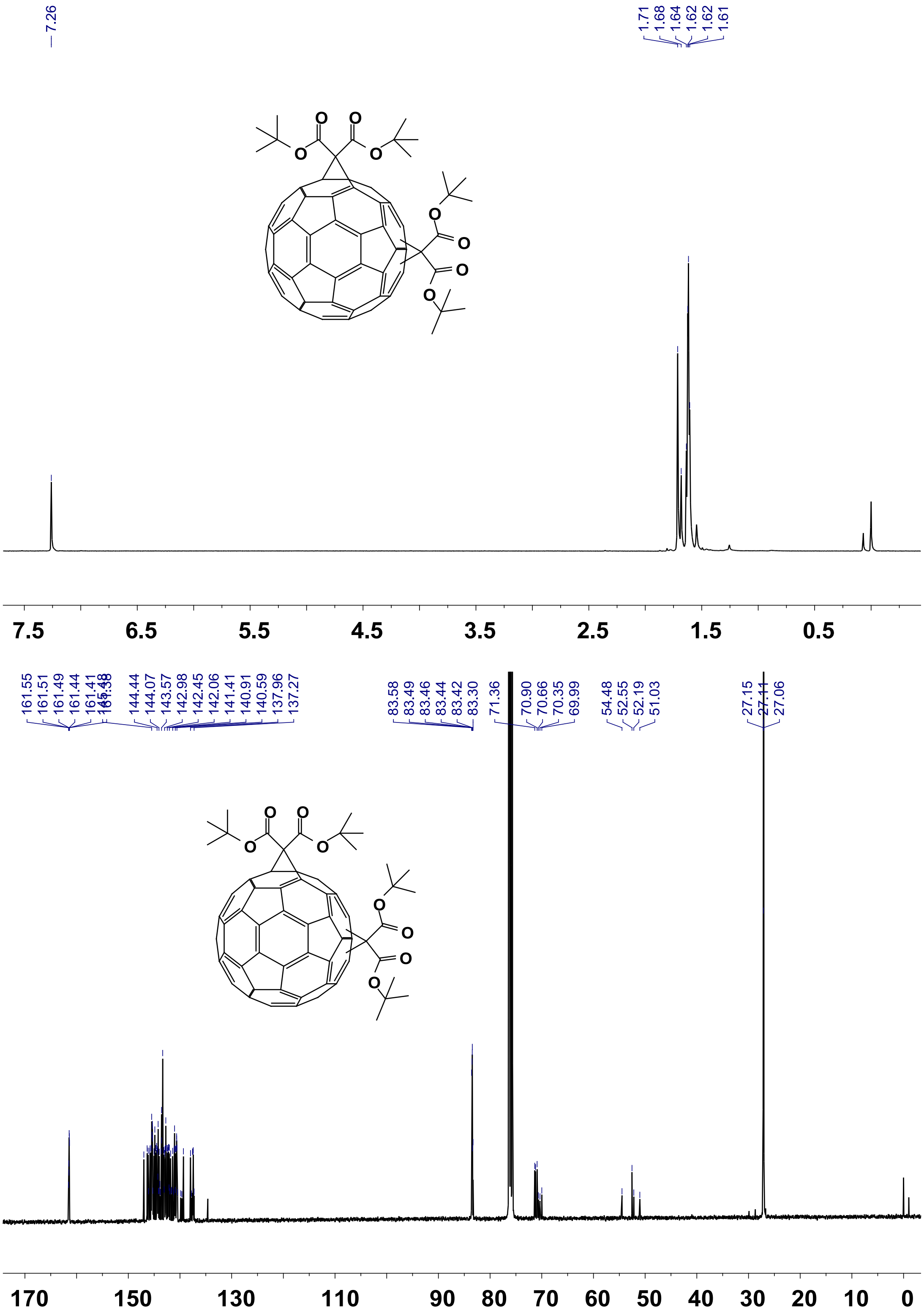


Fig. S3 ^{1}H NMR (in $CDCl_3$, top) and ^{13}C NMR (in $CDCl_3$, bottom) of bis-DBMD.

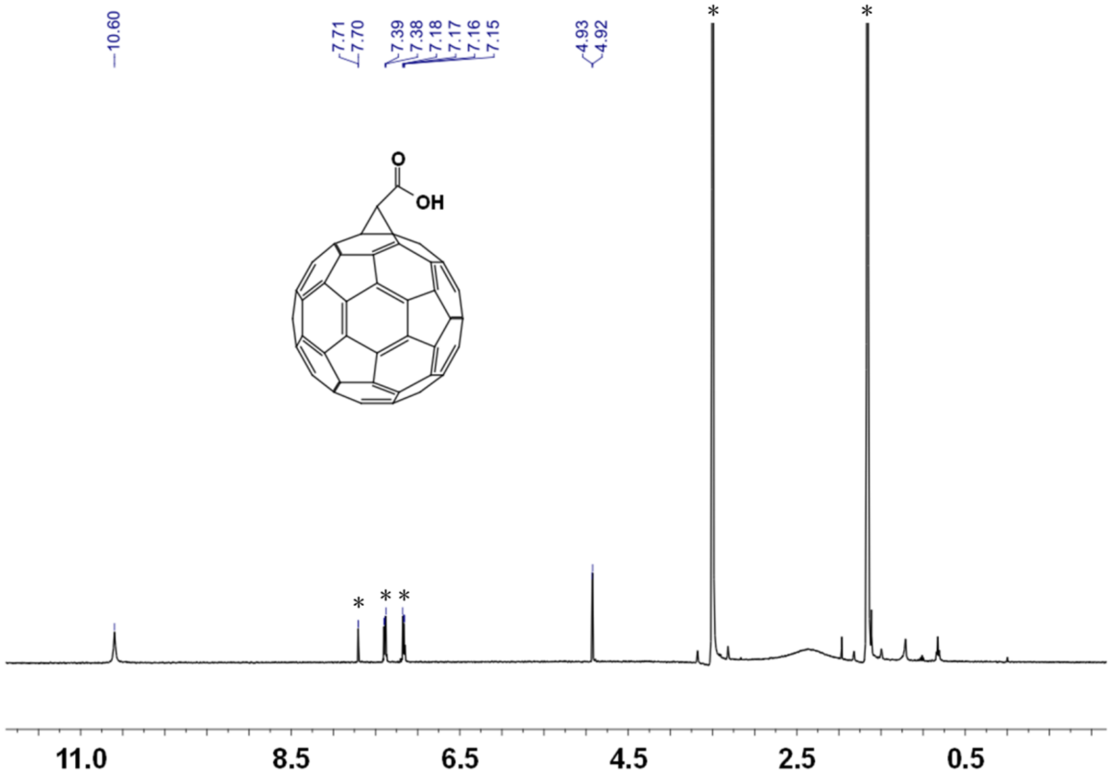


Fig. S4 ^{1}H NMR of MCA1 (in THF-d_8/CS_2/$CDCl_3$/ODCB-d_4)

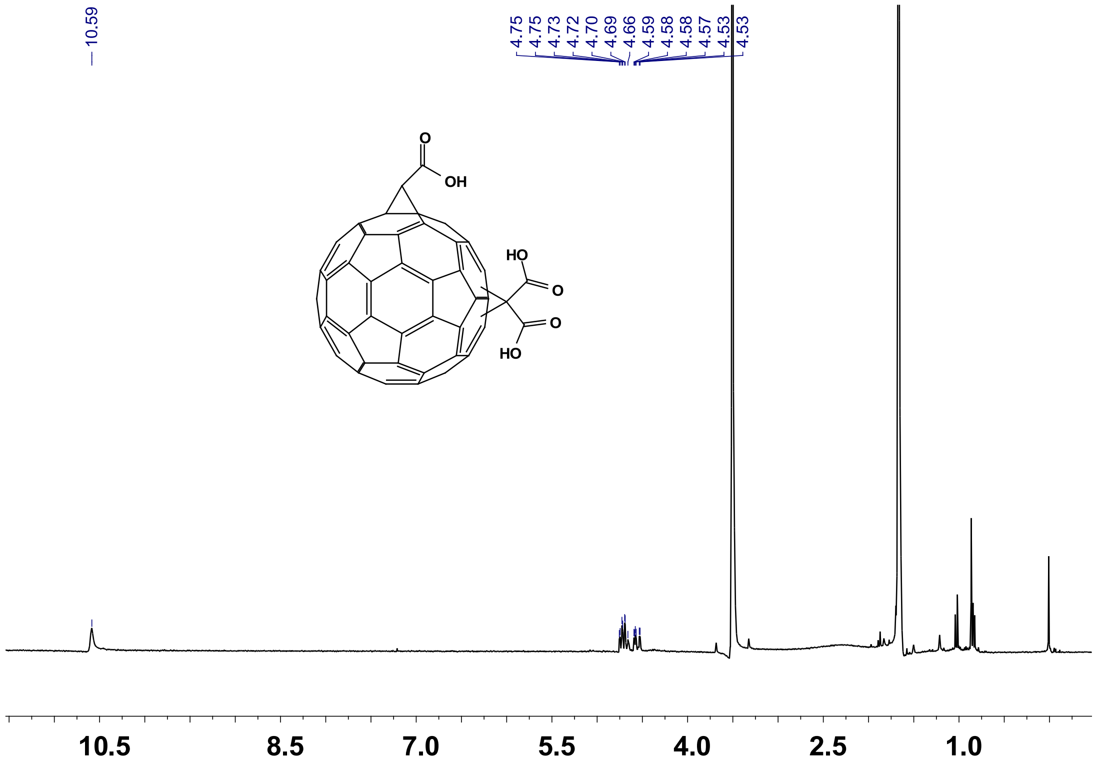
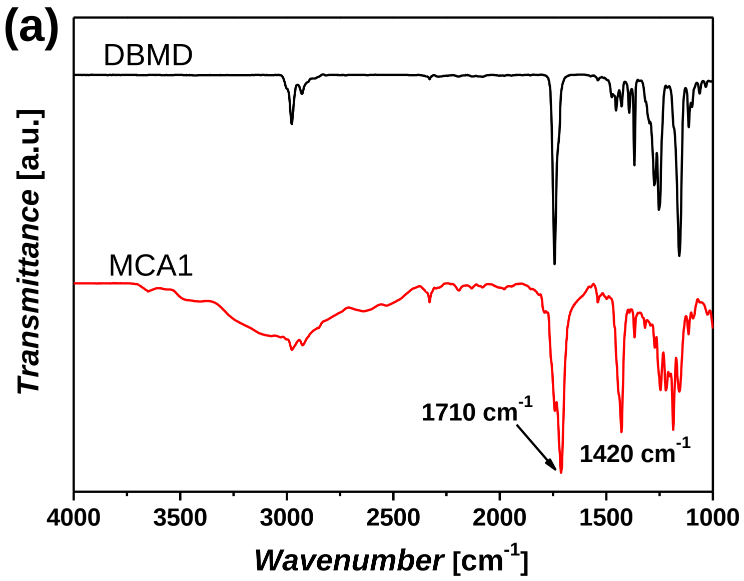
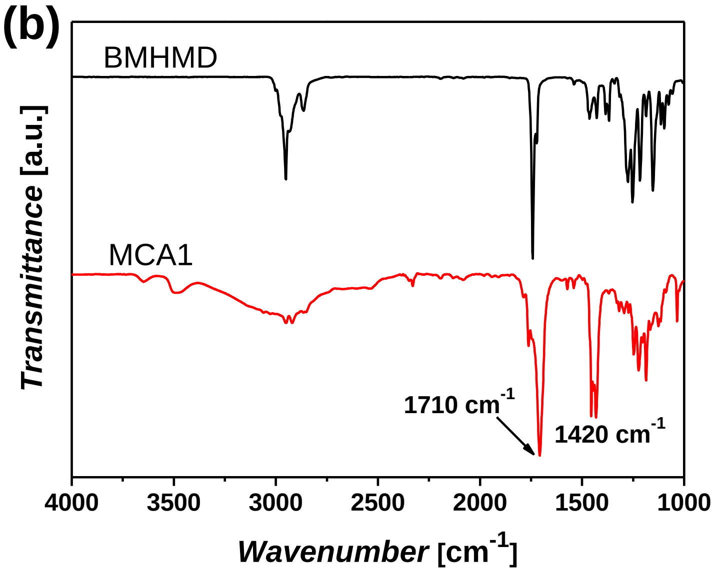


Fig. S5 ^{1}H NMR of MCA2 (in THF-d_8/CS_2).

4. IR spectra


(a)
DBMD
MCA1
1710 cm-1
1420 cm-1
Transmittance [a.u.]
4000
3500
3000
2500
2000
1500
1000
Wavenumber [cm-1]


(b)
BMHMD
MCA1
1710 cm-1
1420 cm-1
Transmittance [a.u.]
4000
3500
3000
2500
2000
1500
1000
Wavenumber [cm-1]

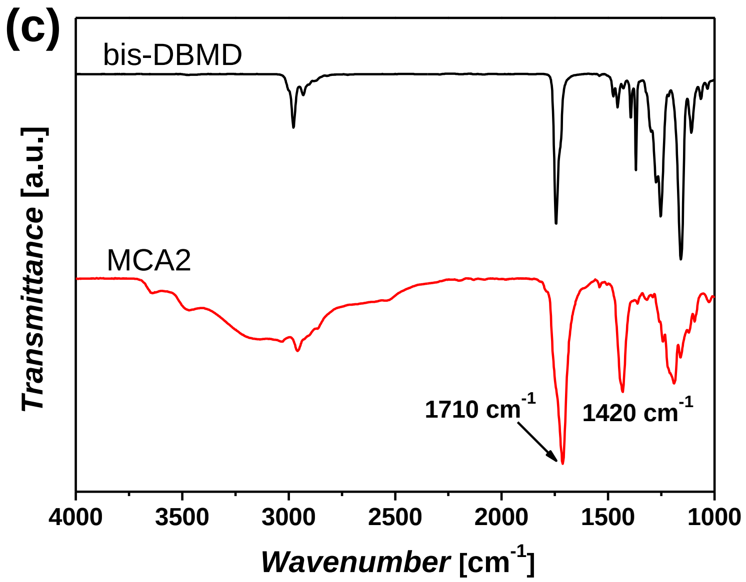


Fig. S6 IR spectra for (a) DBMD and MCA1, (b) BMHMD and MCA1, and (c) bis-DBMD and MCA2.

5. CV measurements

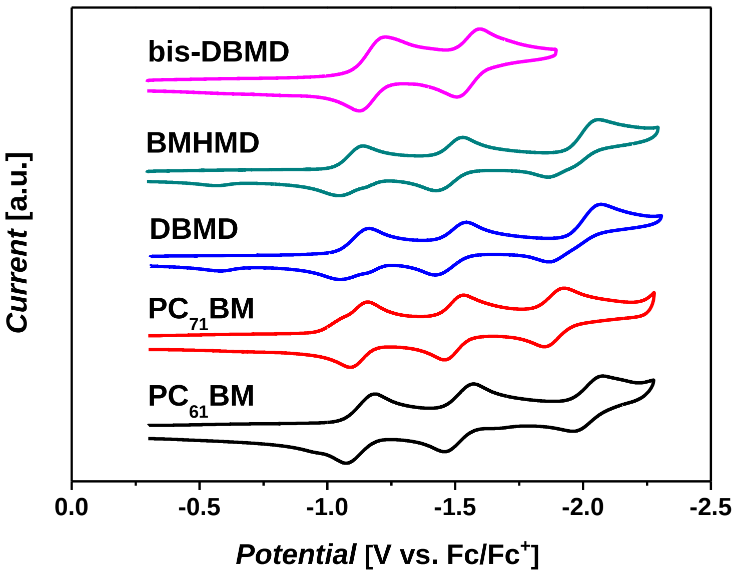


Fig. S7 Cyclic voltammograms of DBMD, BMHMD, bis-DBMD, $PC_{61}BM$, and $PC_{71}BM$.

Table S1 Half-wave reduction potentials and LUMO energy levels of DBMD, BMHMD, bis-DBMD, $PC_{61}BM$, and $PC_{71}BM$.

Fullerenes	$E_{1/2}^{Red1}$ [V]	$E_{1/2}^{Red2}$ [V]	$E_{1/2}^{Red3}$ [V]	LUMO[a] [eV]
DBMD	-1.11	-1.48	-1.97	-3.69
BMHMD	-1.09	-1.48	-1.96	-3.71
bis-DBMD	-1.18	-1.55	---	-3.62
$PC_{61}BM$	-1.13	-1.51	-2.01	-3.67
$PC_{71}BM$	-1.12	-1.50	-1.89	-3.68

[a] LUMO level = $-(E_{1/2}^{Red1} + 4.8)$ eV [4]

6. Effect of MCA1 in active layer on device performance

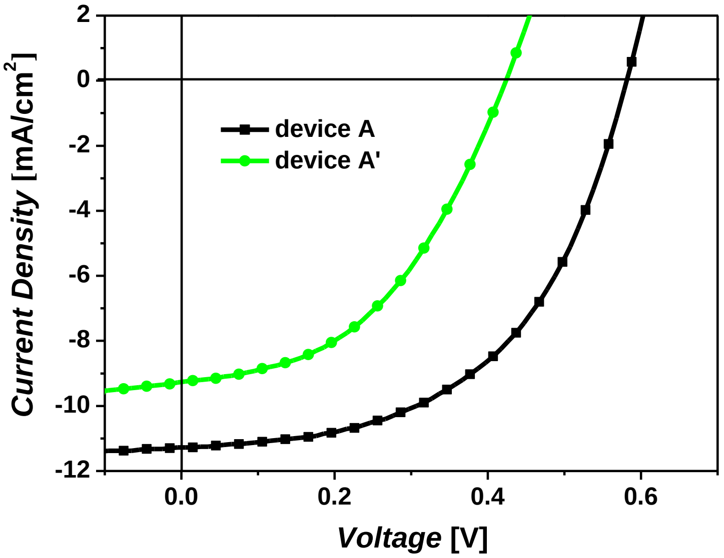


Fig. S8 *J*-*V* curves for ITO/ZnO/P3HT:$PC_{61}BM$ (1:1, w/w)/MoO_3/Ag (device A) and ITO/ZnO/P3HT:$PC_{61}BM$:MCA1 (17:17:0.1, w/w/w)/MoO_3/Ag (device A').

Device	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
A	0.58	11.3	53	3.44
A'	0.42	9.3	45	1.78

7. AFM images

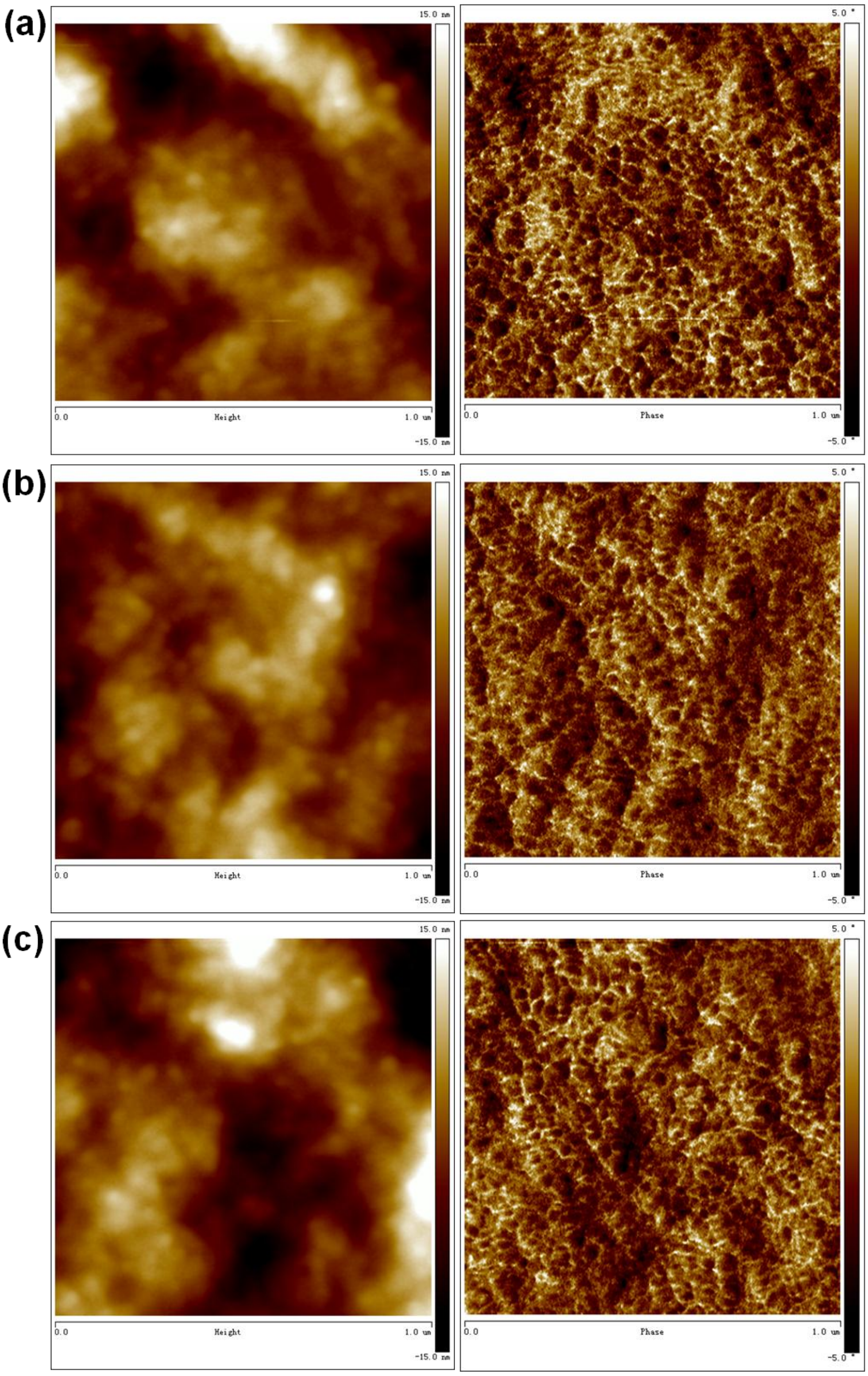


Fig. S9 AFM height (left) and phase (right) images of P3HT/$PC_{61}BM$ blend films: (a) on ZnO, (b) on MCA1-modified ZnO, and (c) on MCA2-modified ZnO (1.0 μm × 1.0 μm).

References

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