Electronic Supplementary Information

_N_-Phenyl[60]fulleropyrrolidines: $PC_{61}BM$-Alternative Acceptor Material for High-Performance Organic Photovoltaic Cell

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Synthesis:

C_{60}-fused *N*-phenyl-2-(4-methoxy-4-oxobutyl)pyrrolidine (**1**)

A toluene solution (150 mL) of methyl 4-formylbutanoate (65 mg, 0.5 mmol), *N*-phenylglycine (151 mg, 1.0 mmol), and [60]fullerene (350 mg, 0.5 mmol) was stirred at 100 °C for 17 h and concentrated under reduced pressure. The product was separated by column chromatography (SiO_2, *n*-hexane:toluene, 2:1) and by preparative GPC to give compound **1** (176 mg, 37%); ^{1}H NMR (400 MHz, $CDCl_3$): 2.04-2.22 (2H, m), 2.45-2.57 (3H, m), 2.60-2.72 (1H, m), 3.71 (3H, s), 5.08 (1H, d, J = 10.6 Hz), 5.40 (1H, d, J = 10.6 Hz), 5.69 (1H, dd, J = 5.5, 7.3 Hz), 7.01 (1H, t, J = 7.3 Hz), 7.31 (2H, d, J = 7.8 Hz), 7.45 (2H, dd, J = 7.3, 7.8Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 23.48, 32.19, 34.10, 51.80, 59.82, 70.60, 70.84, 74.89, 116.54, 120.03, 129.82, 135.67, 135.72, 136.77, 137.34, 139.94, 140.23, 140.30, 140.36, 141.71, 141.79, 142.10, 142.12, 142.17, 142.19, 142.24, 142.31, 142.38, 142.41, 142.44, 142.74, 142.83, 143.24, 144.51, 144.53, 144.71, 145.27, 145.34, 145.40, 145.43, 145.46, 145.50, 145.57, 145.77, 145.81, 146.10, 146.12, 146.22, 146.32, 146.36, 146.40, 146.71, 147.04, 147.38, 147.42, 151.81, 154.00, 155.72, 155.87, 173.60.; UV–vis ($CHCl_3$): λ_{max} (ε) = 257 nm (102000); MS (FAB) m/z 940 (M+1); HRMS calcd for $C_{73}H_{17}NO_2$: 939.12593; found: 939.1278; Anal. Calcd. C 93.28, H 1.82, N 1.49; Found C 93.38, H 2.10, N 1.60.

Methyl 4-((2-*tert*-butoxy)-2-oxoethylamino)butanoate

A solution of *t*-butyl bromoacetate (1.95 g, 10.0 mmol) in anhydrous THF (10 mL) was added dropwise at 0 °C to the mixture of methyl 4-aminobutanoate hydrochloride (1.53 g, 10.0 mmol) and triethylamine (2.02 g, 20.0 mmol) in anhydrous THF (30 mL). The solution was stirred at room temperature for 13 h, then poured into water, and extracted with diisopropyl ether. The organic layer was washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.47 (9H, s), 1.36 (1H, bs), 1.81 (2H, quint, J = 7.3 Hz), 2.39 (2H, t, J = 7.3 Hz), 2.63 (2H, t, J = 7.3 Hz), 3.28 (2H, s), 3.67 (3H, s); MS (FAB) m/z 232 (M+1): HRMS calcd for $C_{11}H_{22}NO_4$: 232.1549; found: 232.1543.

2-(4-methoxy-4-oxobutylamino)acetic acid trifluoroacetic acid salt

After evaporation of the solvent of the above-described compound, the product was diluted with anhydrous CH_2Cl_2 (10 mL), and added with trifluoroacetic acid (4.5 mL). The mixture was stirred at room temperature for 20 h and concentrated under reduced pressure to give the title compound as a colorless viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.02-2.11 (2H, m), 2.15-2.25 (2H, m), 2.64 (2H, t, J = 7.8 Hz), 3.67 (3H, s), 4.20 (2H, s); MS (FAB) m/z 176 (M+1): HRMS calcd for $C_7H_{14}NO_4$: 176.0923; found: 176.0919.

C_{60}-fused *N*-(4-methoxy-4-oxobutyl)-2-phenylpyrrolidine (**2**)

A solution of the above-described trifluoroacetic acid salt of the amino acid (474 mg) in anhydrous toluene (200 mL) was added dropwise at 100 °C to a mixture of benzaldehyde (53 mg, 0.5 mmol), triethylamine (202 mg, 2.0 mmol), and [60]fullerene (360 mg, 0.5 mmol) in anhydrous toluene (100 mL). The mixture was stirred at 110 °C for 20 h and concentrated under reduced pressure. The product was separated by column chromatography (SiO_2, toluene) and by preparative GPC to give the compound **2** (58 mg, 12%); ^{1}H NMR (400 MHz,

$CDCl_3$, δ): 2.14-2.28 (1H, m), 2.28-2.42 (1H, m), 2.62-2.70 (2H, m), 2.76-2.88 (1H, m), 3.20-3.29 (1H, m), 3.76 (3H, s), 4.11 (1H, d, J = 9.2 Hz), 5.08 (1H, s), 5.12 (1H, d, J = 9.2 Hz), 7.10-7.43 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 23.48, 31.99, 51.77, 52.18, 66.62, 68.85, 76.57, 82.50, 128.53, 135.67, 135.80, 136.49, 136.74, 137.09, 139.39, 139.83, 140.14, 140.18, 141.49, 141.67, 141.80, 141.89, 141.96, 142.01, 142.06, 142.08, 142.14, 142.24, 142.26, 142.53, 142.55, 142.67, 142.97, 143.14, 144.36, 144.39, 144.59, 144.70, 145.12, 145.21, 145.26, 145.30, 145.35, 145.47, 145.50, 145.52, 145.73, 145.91, 145.93, 146. 08, 146.11, 146.15, 146.20, 146.25, 146.29, 146.44, 146.75, 147.29, 153.40, 154.12, 174.02; UV–vis ($CHCl_3$): λ_{max} (ε) = 257 nm (104000); MS (FAB) m/z 940 (M+1): HRMS calcd for $C_{73}H_{17}NO_2$: 939.12593; found: 939.1245; Anal. Calcd. C 93.28, H 1.82, N 1.49; Found C 93.34, H 2.05, N 1.56..

C_{60}-fused *N*-dodecyl-2-(4-methoxy-4-oxobutyl)pyrrolidine (**3**)

A toluene solution (100 mL) of methyl 4-formylbutanoate (32 mg, 0.25 mmol), *N*-laurylglycine (122 mg, 0.5 mmol), and C_{60} (175 mg, 0.25 mmol) was stirred at 110 °C for 24 h and concentrated under reduced pressure. The product was separated by column chromatography (SiO_2, toluene) to give the compound **3** (121 mg, 47%); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.89 (3H, t, J = 6.8 Hz), 1.23-1.70 (12H, m), 1.85-2.03 (2H, m), 2.17-2.30 (2H, m), 2.38-2.60 (4H, m), 2.82-2.93 (1H, m), 3.48-3.60 (1H, m), 3.68 (3H, s), 4.13 (1H, d, J = 10.1 Hz), 4.16 (1H, dd, J = 5.5, 4.6 Hz), 4.92 (1H, d, J = 10.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.27, 22.82, 22.96, 27.79, 28.82, 29.50, 29.82, 29.83, 30.64, 32.05, 34.48, 51.74, 52.78, 66.91, 70.88, 76.34, 77.02, 77.31, 135.51, 135.78, 136.27, 137.30, 139.73, 140.01, 140.27, 140.33, 141.82, 141.86, 141.92, 142.13, 142.14, 142.19, 142.24, 142.26, 142.34, 142.70, 142.72, 142.75, 143.15, 143.29, 144.49, 144.52, 144.65, 144.81, 145.28, 145.31, 145.33, 145.36, 145.38, 145.41, 145.48, 145.67, 145.76, 145.84, 146.04, 146.06, 146.11, 146.16, 146.22, 146.24, 146.33, 146.37, 146.56, 146.61, 147.26, 147.29, 153.46, 154.90, 155.15,

156.73, 173.79; UV–vis ($CHCl_3$): λ_{max} (ε) = 257 nm (117000); Calcd. for $C_{79}H_{37}NO_2$: 1032.145: Anal. C 91.93, H 3.61, N 1.36; Found: C 91.64, H 3.62, N 1.41.

C_{60}-fused *N*-phenyl-2-phenylpyrrolidine (**4**)

A toluene solution (100 mL) of benzaldehyde (28.5 mg, 0.25 mmol), *N*-phenylglycine (76 mg, 0.5 mmol), and [60] fullerene (175 mg, 0.25 mmol) was stirred at 110 °C for 24 h and concentrated under reduced pressure. The product was separated by column chromatography (SiO_2, *n*-hexane:toluene, 10:1) to give the compound **4** (78 mg, 34%); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.00 (1H, d, *J* = 10.5 Hz), 5.68 (1H, d, *J* = 10.5 Hz), 6.08 (1H, s), 7.02-7.10 (1H, m), 7.22-7.40 (7H, m), 7.70-7.81 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 68.21, 68.61, 121.50, 122.37, 128.26, 128.65, 128.84, 129.19, 135.72, 135.80, 136.54, 137.79, 139.35, 139.89, 140.21, 140.30, 141.58, 141.75, 141.86, 141.91, 142.06, 142.07, 142.12, 142.15, 142.18, 142.27, 142.28, 142.63, 142.74, 143.06, 143.19, 144.45, 144.62, 144.73, 145.18, 145.29, 145.32, 145.36, 145.48, 145.49, 145.61, 145.75, 146.00, 146.09, 146.14, 146.19, 146.28, 146.29, 146.30, 146.40, 146.68, 153.27, 153.46, 153.80, 155.82; UV–vis ($CHCl_3$): λ_{max} (ε) = 257 nm (115000); MS (FAB) m/z 916 (M+1): HRMS calcd for $C_{74}H_{13}N$: 915.10480; found: 915.1039; the sample for elemental analysis was obtaind as **4**:toluene = 1:1, which was confirmed by its ^{1}H NMR spectrum, Anal. Calcd. for $C_{81}H_{21}N$: C 96.51, H 2.10, N 1.39; Found: C 96.46, H 2.01, N 1.53.

C_{60}-fused *N*-phenyl-2-hexylpyrrolidine (**5**)

A chlorobenzene solution (100 mL) of heptanal (28.5 mg, 0.25 mmol), *N*-phenylglycine (76 mg, 0.5 mmol), and [60] fullerene (175 mg, 0.25 mmol) was stirred at 110 °C for 24 h and concentrated under reduced pressure. The product was separated by column chromatography (SiO_2, *n*-hexane:toluene, 10:1) and by preparative GPC to give the compound **5** (58 mg, 25%); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.88 (3H, t, *J* = 6.9 Hz), 1.25-1.40 (4H, m), 1.40-1.60

(2H, m), 1.72-1.86 (2H, m), 2.40-2.52 (1H, m), 2.58-2.70 (1H, m), 5.09 (1H, d, J = 10.5 Hz), 5.39 (1H, d, J = 10.5 Hz), 5.66 (1H, dd, J = 7.8, 5.0 Hz), 7.00 (1H, t, J = 7.3 Hz), 7.30 (2H, d, J = 7.3 Hz), 7.45 (2H, t, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.20, 22.67, 28.11, 29.53, 31.71, 32.52, 59.58, 70.53, 71.06, 74.89, 116.49, 119.74, 125.40, 128.33, 129.14, 129.77, 135.66, 135.76, 136.90, 137.23, 139.83, 140.22, 140.28, 140.33, 141.70, 141.79, 142.10, 142.12, 142.14, 142.20, 142.25, 142.29, 142.31, 142.40, 142.47, 142.73, 142.83, 143.24, 144.53, 144.72, 145.33, 145.39, 145.43, 145.45, 145.59, 145.77, 145.82, 146.09, 146.11, 146.32, 146.34, 146.40, 146.52, 146.82, 147.15, 147.37, 147.40, 152.25, 154.09, 155.92, 156.19;UV–vis ($CHCl_3$): λ_{max} (ε) = 257 nm (113000); MS (FAB) m/z 924 (M+1): HRMS calcd for $C_{74}H_{21}N$; 923.16740; found; 923.1707; Anal. Calcd. C 96.19, H 2.29, N 1.52; found C 95.97, H 2.46, N 1.57.

C_{60}-fused *N*-phenyl-2-methoxyethoxyethoxymethylpyrrolidine (**6**)

A chlorobenzene solution (100 mL) of methoxyethoxyethoxymethyl aldehyde (40 mg, 0.25 mmol), *N*-phenylglycine (76 mg, 0.5 mmol), and [60] fullerene (360 mg, 0.5 mmol) was stirred at 120 °C for 48 h and concentrated under reduced pressure. The product was separated by column chromatography (SiO_2, toluene:ethyl acetate, 50:1) and by preparative GPC to give the compound **6** (194 mg, 40%); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.34 (3H, s), 3.45-3.52 (2H, m), 3.52-3.59 (2H, m), 3.59-3.69(3H, m), 3.69-3.77 (1H, m), 3.40 (1H, dd, J = 10.3, 2.8 Hz), 4.59 (1H, dd, J = 10.3, 6.2 Hz), 5.31 (2H,s), 5.84 (1H, dd, J = 6.2, 2.8 Hz), 7.01 (1H, t, J = 7.7 Hz), 7.28 (2H, d, J = 8.0 Hz), 7.47 (2H, dd, J = 8.0, 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 59.20, 60.86, 69.60, 69.72, 70.37, 70.66, 70.75, 70.88, 72.04, 72.91, 116.29, 119.58, 129.82, 135.41, 135.69, 137.24, 137.30, 139.65, 140.16, 140.26, 140.29, 141.72, 141.85, 142.04, 142.10, 142.17, 142.24, 142.33, 142.47, 142.71, 142.84, 143.21, 143.25, 144.59, 144.63, 144.73, 145.30, 145.39, 145.58, 145.72, 145.75, 145.86, 145.93, 146.08, 146.13, 146.18, 146.34, 146.37, 146.40, 146.89, 146.97, 147.44, 147.45, 152.65, 154.05, 156.07; UV–vis

($CHCl_3$): λ_{max} (ε) = 257 nm (129000); MS (FAB) m/z 972 (M+1): HRMS calcd for $C_{74}H_{21}NO_3$: 971.15214; found: 971.1500; Anal. Calcd. C 91.44, H 2.18, N 1.44; Found C 91.42, H 2.35, N 1.55.

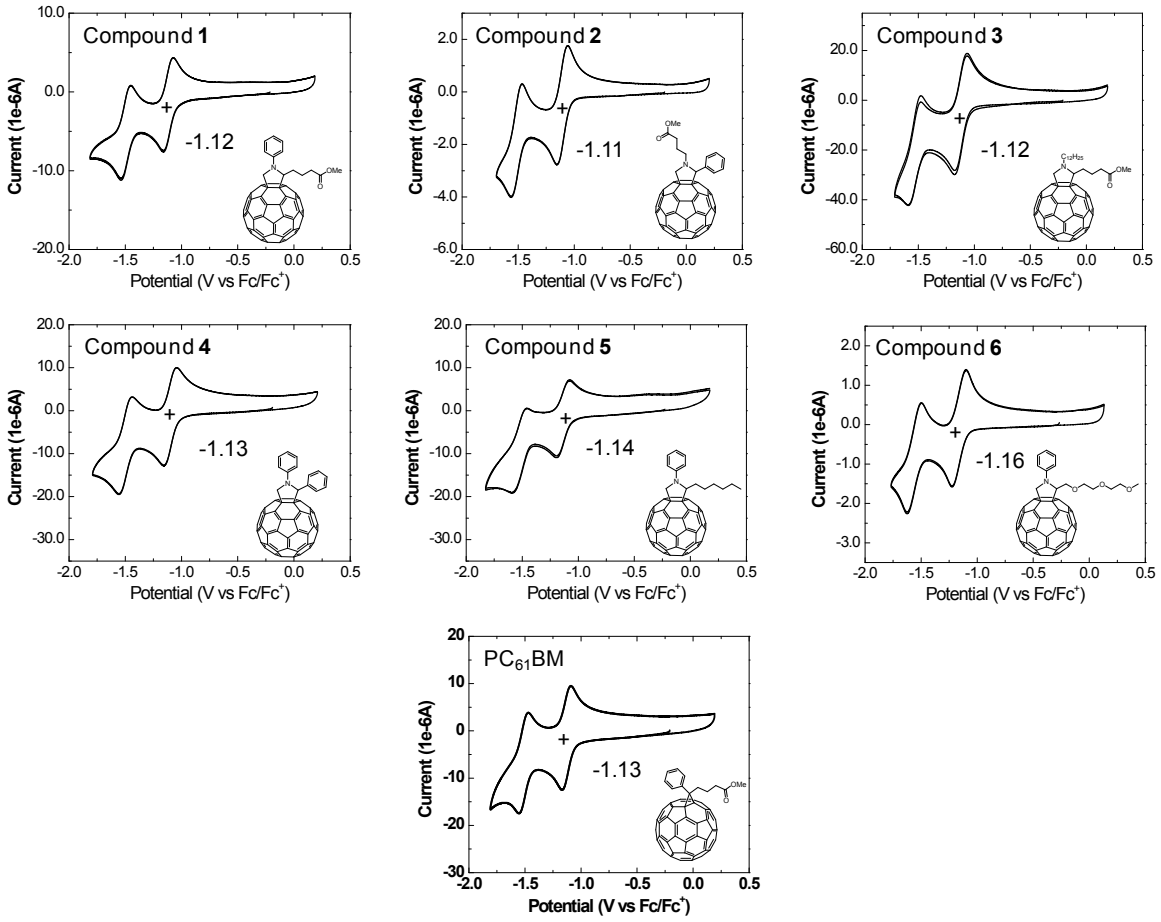

Figure S1. Cyclic voltammograms of fullerene derivatives.

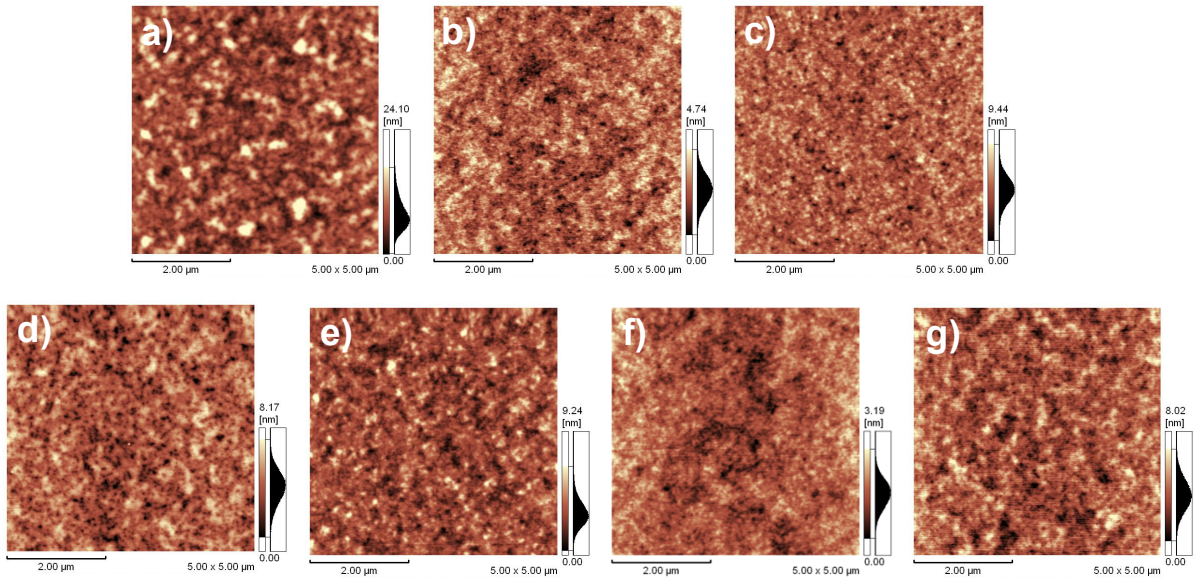

Figure S2. AFM images of blended films for OPV using P3HT and fullerene derivatives; a) compound **1**, b) compound **2**, c) compound **3**, d) compound **4**, e) compound **5**, f) compound **6**, and g) $PC_{61}BM$.

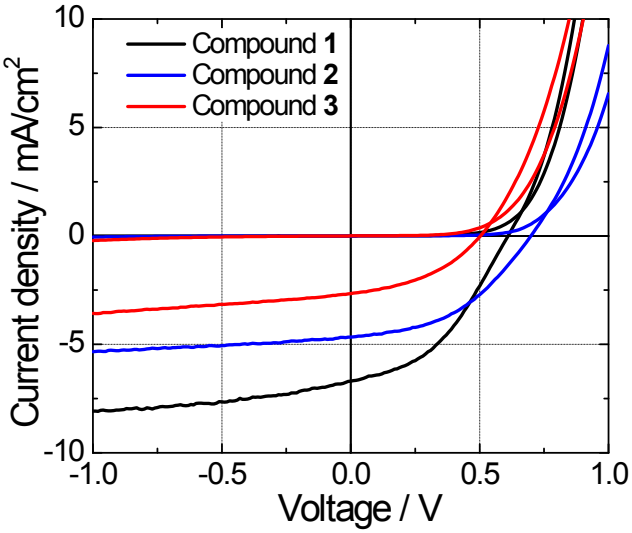

Figure S3. *J–V* curves for OPV device with MoOx layer.

Table S1. Performance data of OPVs using MoOx as a hole transporting layer[a]

Acceptor	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
1	6.702	0.611	0.414	1.69
2	4.661	0.699	0.441	1.44
3	2.664	0.503	0.405	0.54

[a] The device structure is ITO/MoOx/active layer/Al.

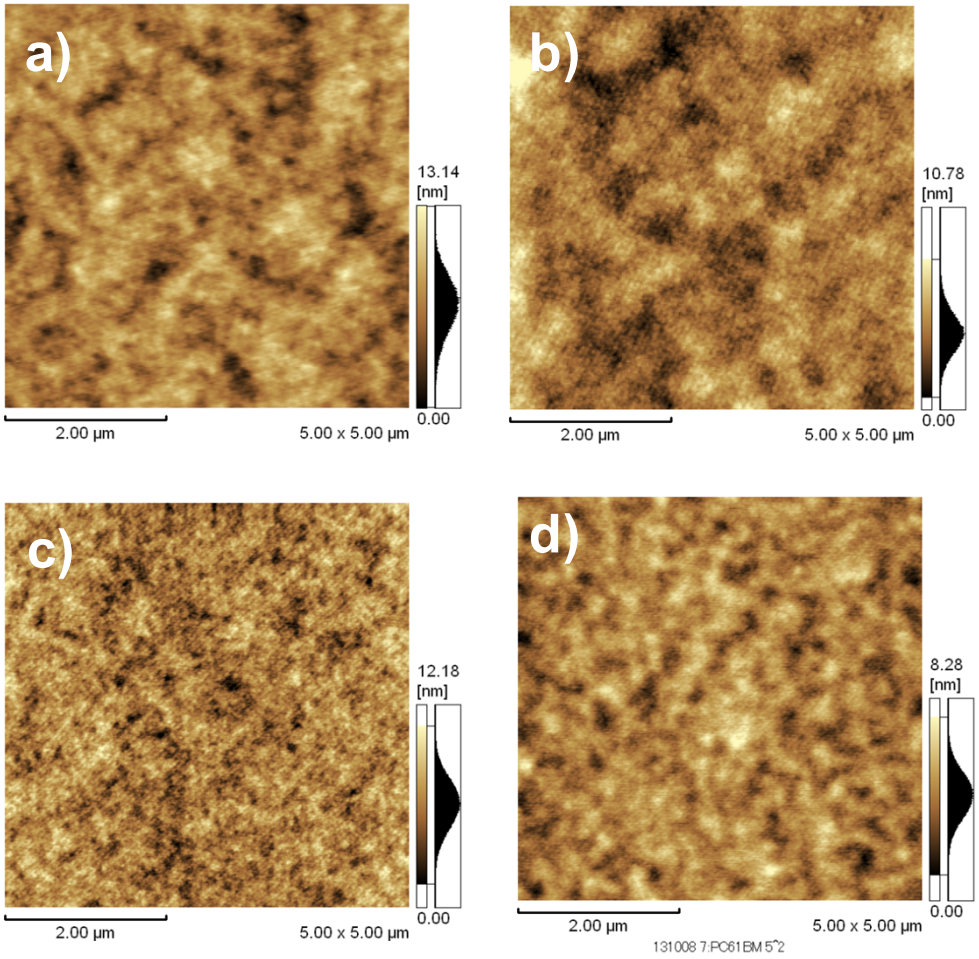

Figure S4. AFM images of blended films for OPV using PTB7 and fullerene derivatives; a) compound **4**, b) compound **5**, c) compound **6**, and d) $PC_{61}BM$.