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Supporting Information

The Role of Fullerene Derivatives in Perovskite Solar Cells: Electron Transporting or Electron Extraction Layers?

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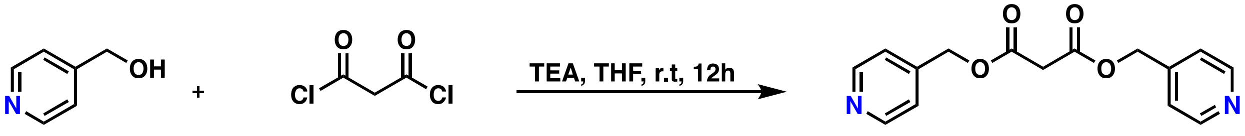
Synthesis methods

*Synthesis of (4-Pyridyl)methyl 3-oxo-4-(4-pyridyl)butyrate (**1**)*

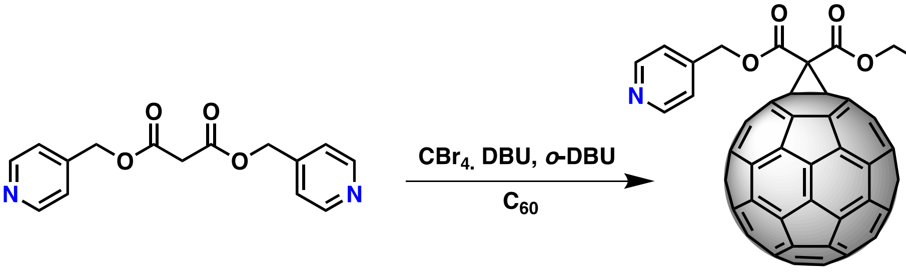


1

In a 2-neck round bottom flask equipped with a magnetic stirrer, 0.69 mL of malonyl chloride (7.09 mmol, 1 eq), were dissolved in 10 mL of dry THF. 1.55g of 4-pyridinemethanol (14.19 mmol, 2 eq) were added to the mixture and then 1.9 mL of triethylamine were added dropwise while stirring. The reaction mixture was left 12h at room temperature. The crude reaction mixture was filtered, washed with acetone dried under vacuum. The purification was performed by column chromatography using a mixture of chloroform : methanol (20:1→ 8:2) to obtain the product, 19% yield. [m/z + H^+]calc. =287.1026, [m/z + H^+]exp. =287.1012

^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ(ppm): 8.48 (d, *J* = 5.8 Hz, 2H), 7.15 (d, *J* = 5.4 Hz, 2H), 5.11 (s, 2H), 3.52 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 298K) δ(ppm): 165.7, 149.8, 144.2, 122.0, 65.2, 41.0.

Synthesis of BPy-C₆₀

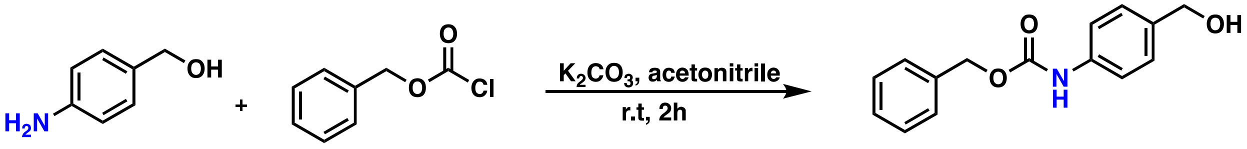


BPy-C₆₀

In a round bottom flask equipped with a magnetic stirrer, **1** (36 mg, 0.13 mmol, 1.3 eq), C_{60} (72 mg, 0.1 mmol, 1 eq) and CBr_4 (43.11 mg, 0.13 mmol, 1.3 eq) were dissolved in 10 mL of *o*-DCB. After keeping the mixture in ultrasonication for 30 min, one drop of DBU was added to the reaction under stirring and left to react for 2 minutes. The reaction crude was inmediately purified by column chromatography using CS_2 to remove the unreacted C_{60} and a mixture of chloroform : methanol (20:1→ 8:2) to obtain the product, 28% (93%) yield. [m/z + H^+]calc. =1004.19, [m/z + H^+]exp.= 1005.1143.

^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ(ppm): 8.66 (d, *J* = 6.0 Hz, 4H), 7.36 (d, *J* = 5.9 Hz, 4H), 5.52 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$, 298K) δ(ppm): 163.1, 150.4, 145.4, 145.3, 144.9, 144.8, 144.5, 143.9, 143.1, 142.2, 141.8, 141.08, 139.1, 129.1, 128.3, 122.5, 66.9, 30.9.

Synthesis of benzyl 4-(hydroxymethyl)phenylcarbamate (2)



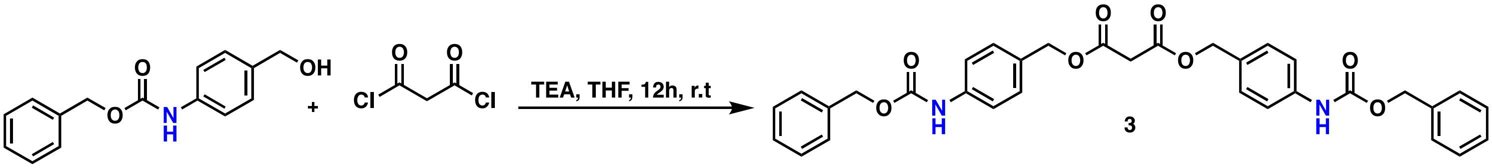
2

In a round bottom flask equipped with a magnetic stirrer, 1g of 4-aminobenzyl alcohol (8 mmol, 1 eq) and 1.12g of potassium carbonate (8 mmol, 1 eq) were dissolved in 15 mL of dry acetonitrile. Benzyl chloroformate (1.16 mL, 8 mmol, 1 eq) was dissolved in 5 mL of acetonitrile and added to the reaction mixture dropwise in a period of time of 5 minutes. The reaction mixture was left stirring 2h at room temperature. After that period of time the reaction was quenched with 6mL of

$NaHCO_3$ (conc) and 6 mL of NaCl (sat). The reaction crude was filtered, dried under vacuum and purified by column chromatography using a mixture of ethyl acetate : hexane (2:1) to obtain the product, 77% yield. [m/z + H^+]calc. =258.1125, [m/z + H^+]exp.= 258.1132

^1H NMR (600 MHz, $CDCl_3$, 298K) δ(ppm): 7.43 – 7.25 (m, 10H), 6.74 (s, 1H), 5.19 (s, 2H), 4.62 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, 298K) δ(ppm): 155.8, 153.64, 137.3, 136.1, 128.7, 128.5, 128.4, 128.3, 127.9, 118.9, 67.5, 67.0, 64.8, 53.7, 31.0.

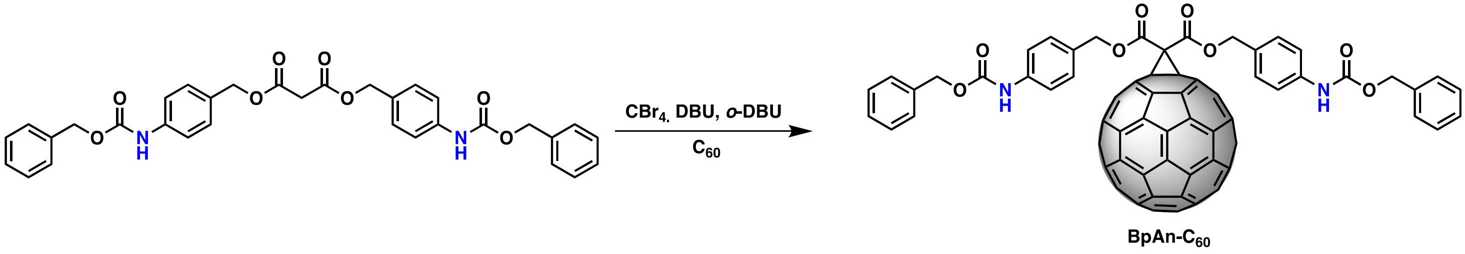
Synthesis of bis(4-(((benzyloxy)carbonyl)amino)benzyl)malonate (3)



In a 2-neck round bottom flask equipped with a magnetic stirrer, 0.14 mL of malonyl chloride (1.42 mmol, 1 eq), were dissolved in 10 mL of dry THF. 0.803g of **2** (3.12 mmol, 2 eq) were added to the mixture and then 0.4 mL of triethylamine were added dropwise while stirring. The reaction mixture was left 12h at room temperature. The reaction crude was filtered, washed with acetone dried under vacuum. The purification was performed by column chromatography using a mixture of ethyl acetate: hexane (2:1) to obtain the product, 37% yield. [m/z + Na^+]calc. =605.1900, [m/z + Na^+]exp. = 605.1890

^1H NMR (600 MHz, $CDCl_3$, 298K) δ(ppm): 7.40 – 7.13 (m, 10H), 5.15 (s, 2H), 5.08 (s, 2H), 3.42 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, 298K) δ(ppm): 167.1, 166.4, 138.1, 135.9, 130.2, 129.5, 129.3, 128.6, 128.4, 128.4, 119.1, 67.1, 67.0, 41.8, 40.8.

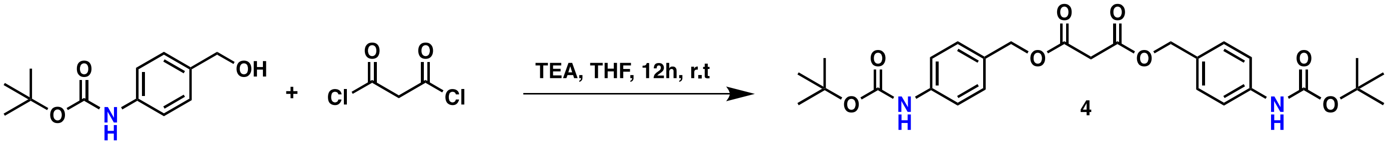
Synthesis of BpAn-C_{60}



In a round bottom flask equipped with a magnetic stirrer, **3** (73 mg, 0.13 mmol, 1.3 eq), C_{60} (72 mg, 0.1 mmol, 1 eq) and CBr_4 (43.11 mg, 0.13 mmol, 1.3 eq) were dissolved in 10 mL of *o*-DCB. After keeping the mixture in ultrasonication for 30 min, one drop of DBU was added to the reaction under stirring and left to react for 2 minutes. The reaction crude was inmediately purified by column chromatography using CS_2 to remove the unreacted C_{60} and a mixture of chloroform : methanol (20:1→ 8:2) to obtain the product, 20% (90%) yield. [m/z + H^+]calc. =1301.1918, [m/z + H^+]exp. = 1301.1935.

^{1}H NMR (600 MHz, $CDCl_3$, 298K) δ(ppm): 7.34 (dddd, *J* = 23.1, 20.7, 12.3, 7.4 Hz, 10H), 6.97 (s, 1H), 5.39 (s, 2H), 5.17 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, 298K) δ(ppm): 163.4, 145.3, 145.3, 145.2, 145.2, 145.1, 145.0, 144.8, 144.7, 143.9, 143.1, 143.1, 143.1, 142.3, 142.0, 141.0, 139.2, 138.4, 135.9, 129.9, 129.8, 128.7, 128.5, 128.4, 119.2, 71.6, 68.7, 67.3, 52.0.

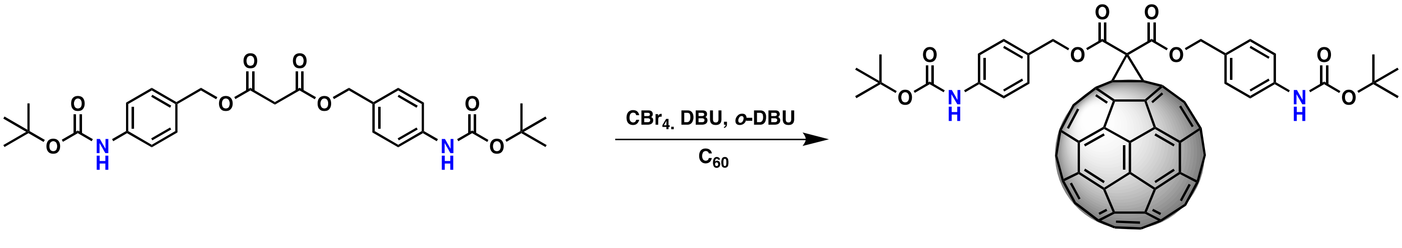
Synthesis of bis(4-(((benzyloxy)carbonyl)amino)tert-butyl)malonate (4)



In a 2-neck round bottom flask equipped with a magnetic stirrer, 0.7 mL of malonyl chloride (7 mmol, 1 eq), were dissolved in 20 mL of dry THF. 3.55 g of 4-bocaminobenzyl alcohol (15 mmol, 2.1 eq) were added to the mixture and then 2 mL of triethylamine were added dropwise while stirring. The reaction mixture was left 12h at room temperature. The reaction crude was filtered, washed with acetone dried under vacuum. The purification was performed by column chromatography using a mixture of ethyl acetate: hexane (1:1) to obtain the product as a yellow waxy solid, 48% yield. [m/z + Na^+]calc. = 537.2213, [m/z + Na^+]exp. = 537.2208.

^{1}H NMR (600 MHz, $CDCl_3$, 298K) δ(ppm): 7.31 (d, *J* = 3.0 Hz, 4H), 7.16 (d, *J* = 7.2 Hz, 4H), 6.92 (s, 4H), 5.05 (s, 4H), 3.40 (s, 2H), 1.49 (s, 18H). ^{13}C NMR (150 MHz, $CDCl_3$, 298K) δ(ppm): 166.6, 153.1, 138.8, 129.4, 118.9, 67.1, 41.9, 28.6.

Synthesis of compound 5

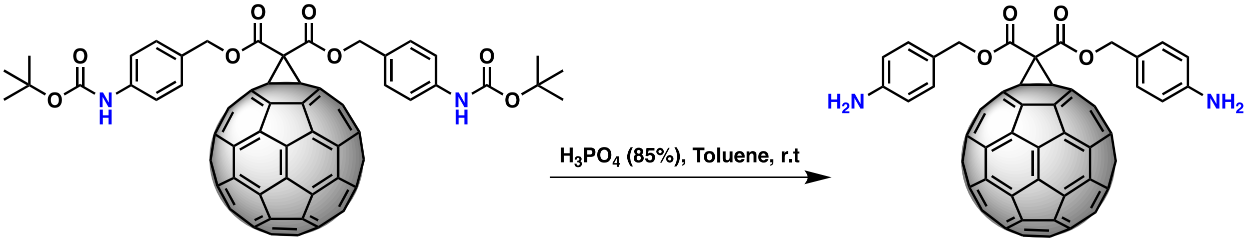


5

In a round bottom flask equipped with a magnetic stirrer, **4** (77 mg, 0.15 mmol, 1.5 eq), C_{60} (72 mg, 0.1 mmol, 1 eq) and CBr_4 (50 mg, 0.15 mmol, 1.5 eq) were dissolved in 10 mL of *o*-DCB. After keeping the mixture in ultrasonication for 30 min, one drop of DBU was added to the reaction under stirring and left to react for 2 minutes. The reaction crude was inmediately purified by column chromatography using CS_2 to remove the unreacted C_{60} and a mixture of chloroform : methanol (20:1→ 8:2) to obtain the product, 17% (83%) yield. [m/z + H^+]calc. = 1235.2388, [m/z + H^+]exp. = 1235.2187.

^{1}H NMR (600 MHz, Toluene-d3, 298K) δ(ppm): 7.20 (d, *J* = 7.2 Hz, 4H), 7.09 (s, 4H), 6.35 (s, 2H), 5.11 (s, 4H), 2.13 (s, 18H). ^{13}C NMR (101 MHz, Toluene-d3) δ(ppm): 163.0, 152.3, 145.3, 145.1, 145.0, 145.00, 144.7, 144.5, 144.4, 143.7, 142.9, 142.7, 142.0, 141.8, 140.7, 139.2, 139.1, 137.4, 136.8, 129.8, 129.1, 118.4, 79.7, 68.6, 29.8, 28.0.

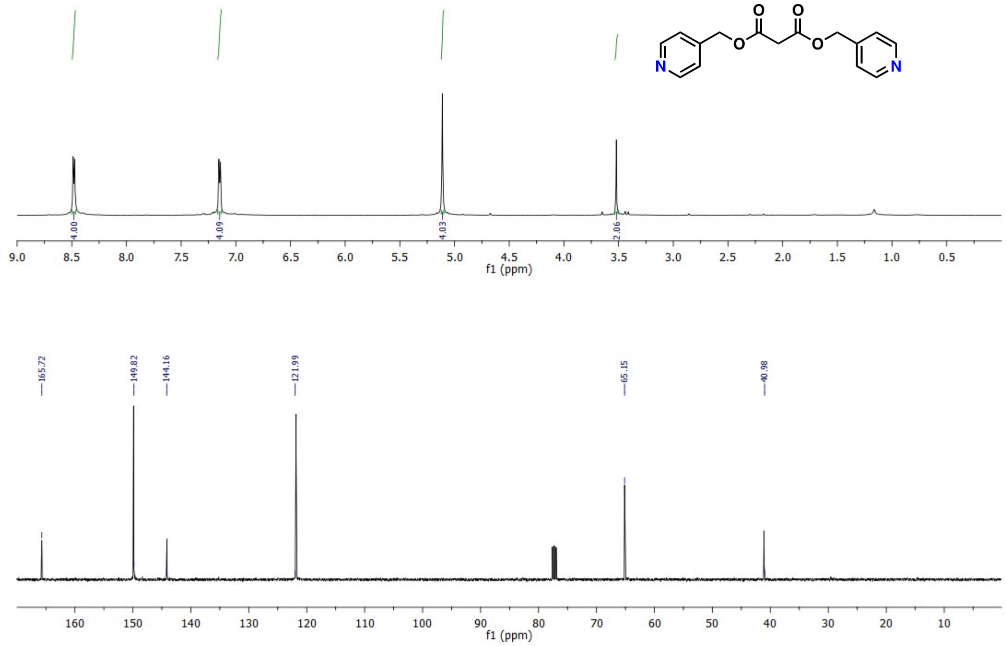
Synthesis of BAn-C_{60}



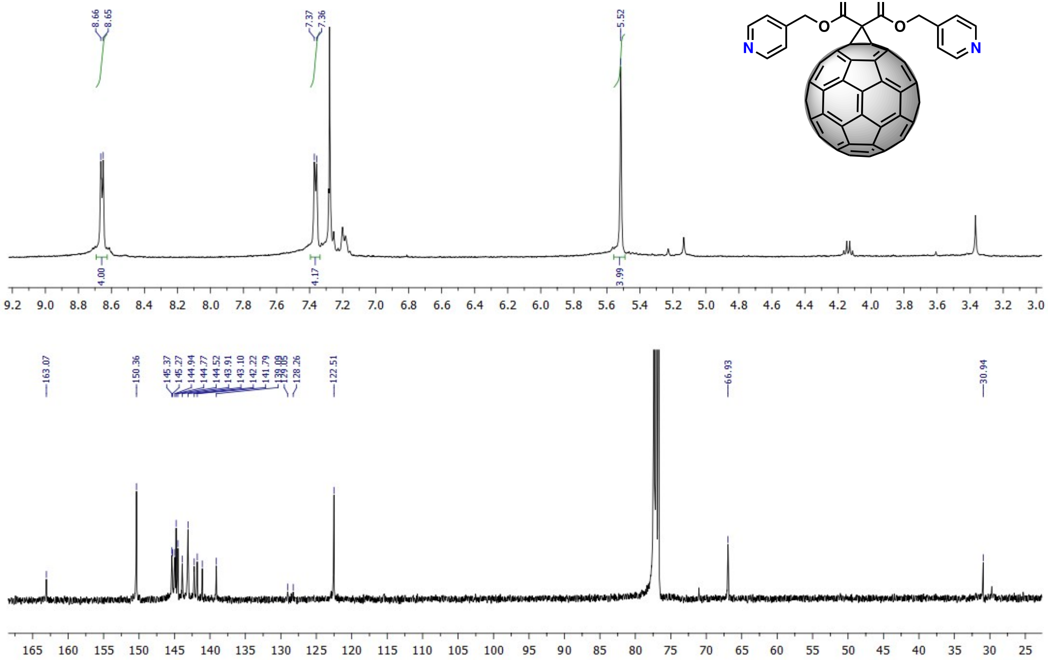
To a solution of 5 (67 mg, 2.95 mmol) in toluene (2 mL) at room temperature was added aqueous phosphoric acid, 85 wt % (26 µL, 0.4 mmol) dropwise. The mixture was vigorously stirred for 12 h. Then 5 mL of water were added and the mixture was cooled to 0 °C. A 50 wt % NaOH solution was added slowly until pH to ~7-8. The mixture was then extracted with $CHCl_3$ (2 × 10 mL). The combined organic phase was dried over magnesium sulfate and concentrated in vacuo. Additional washes with methanol (2 x 5 mL) were required to give the desired product as a brown solid. (97%). [m/z + H^+]calc. = 1033.1188, [m/z + H^+]exp. = 1033.1203.

^{1}H NMR (600 MHz, $CDCl_3$, 298K) δ(ppm): 7.34 (d, *J* = 7.2 Hz, 4H), 7.28 (d, *J* = 6.7 Hz, 4H), 6.73 (s, 4H), 5.36 (s, 4H). ^{13}C NMR (150 MHz, $CDCl_3$, 298K) δ(ppm): 163.5, 152.8, 145.3, 145.2, 145.1, 144.9, 144.8, 144.7, 143.9, 143.1, 142.3, 142.0, 141.0, 139.2, 139.0, 130.1, 129.1, 118.8, 71.5, 68.3, 30.1.

^{1}H and ^{13}C NMR Characterization



a) (4-Pyridyl)methyl 3-oxo-4-(4-pyridyl)butyrate (1)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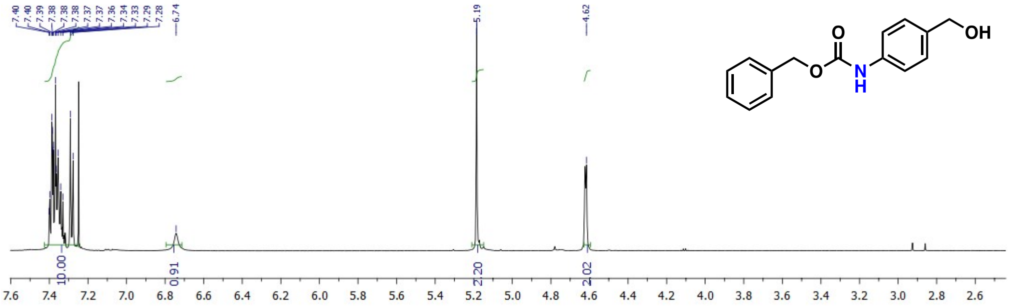
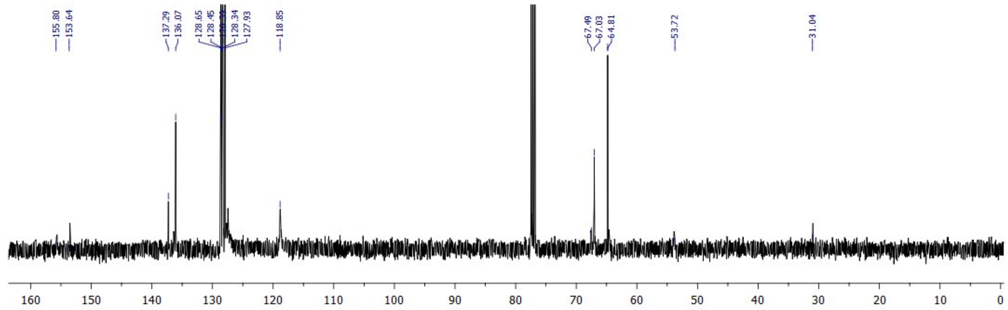
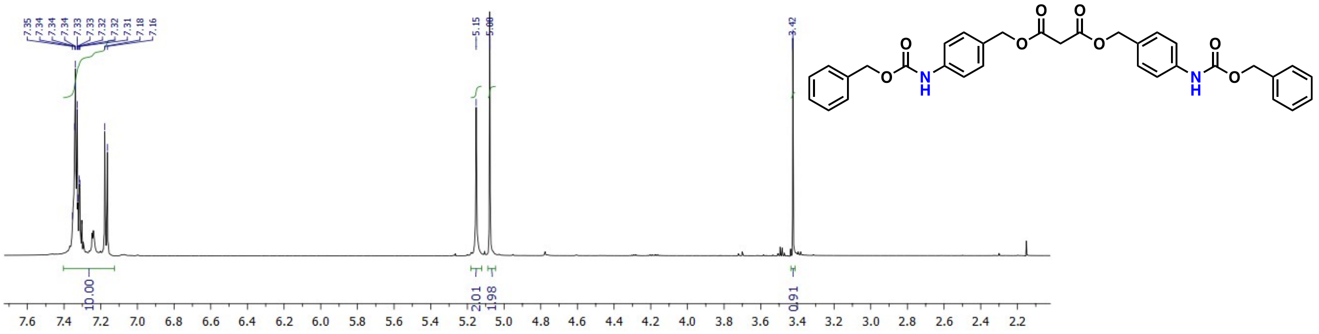
b) BPy-C_{60}

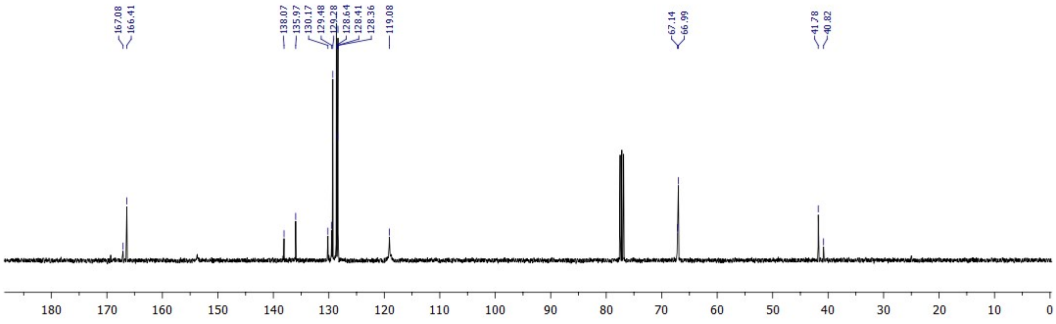
c) Benzyl 4-(hydroxymethyl)phenylcarbamate (2)



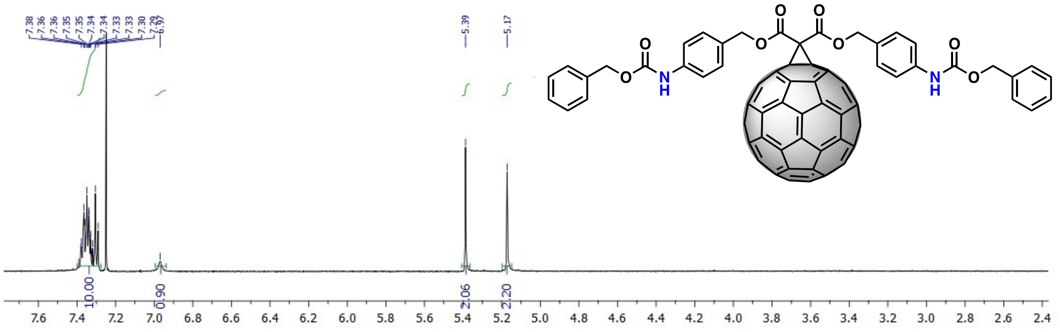


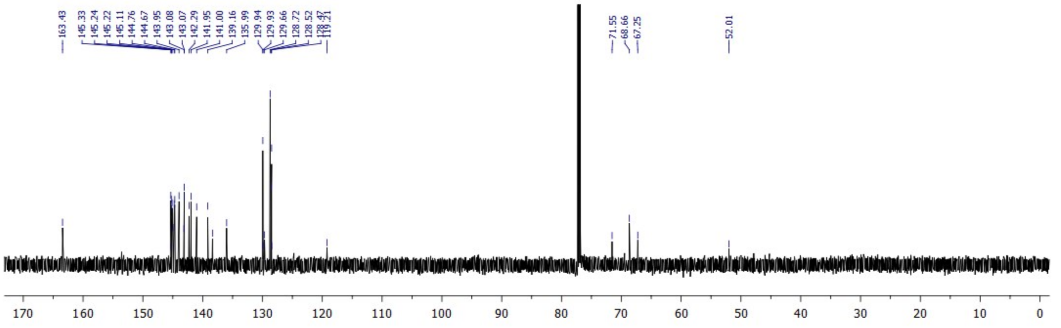
d) Bis(4-(((benzyloxy)carbonyl)amino)benzyl)malonate (3)



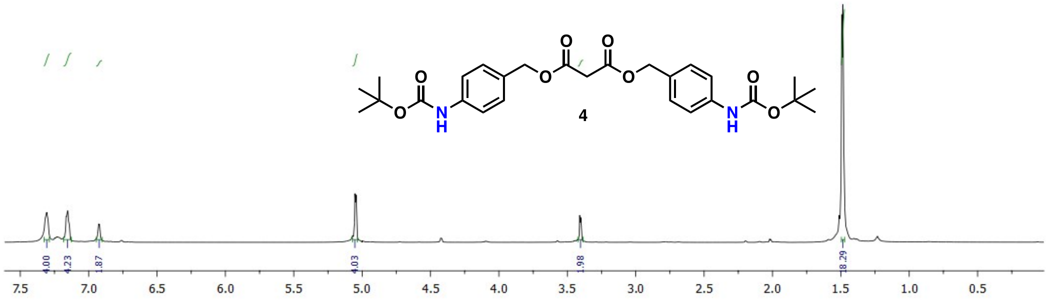


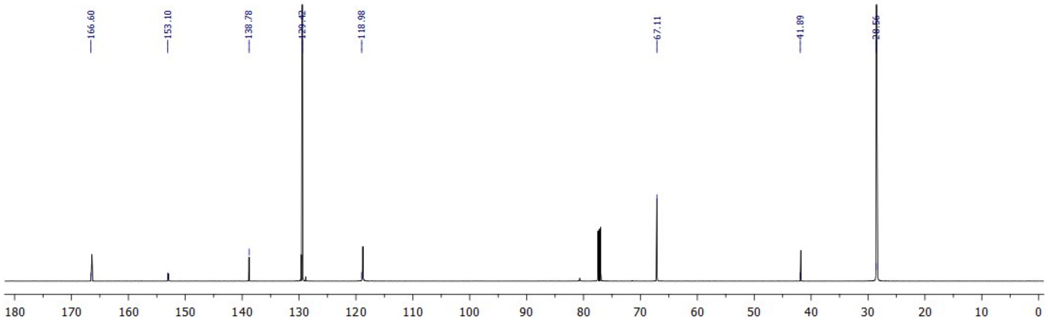
e) BpAn-C_{60}



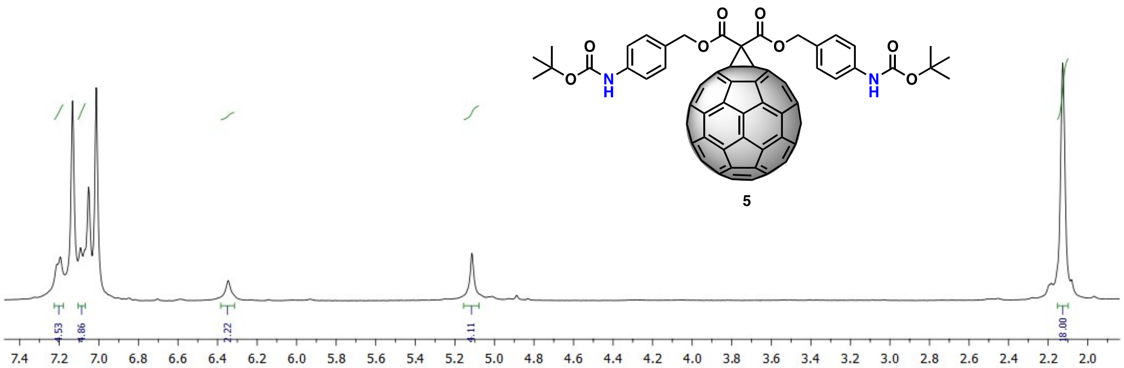


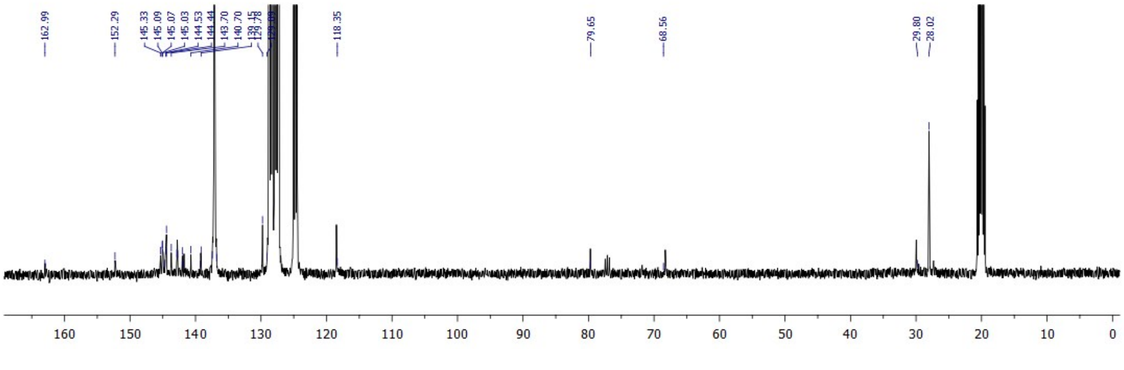
f) Bis(4-(((benzyloxy)carbonyl)amino)tertbutyl)malonate (4)



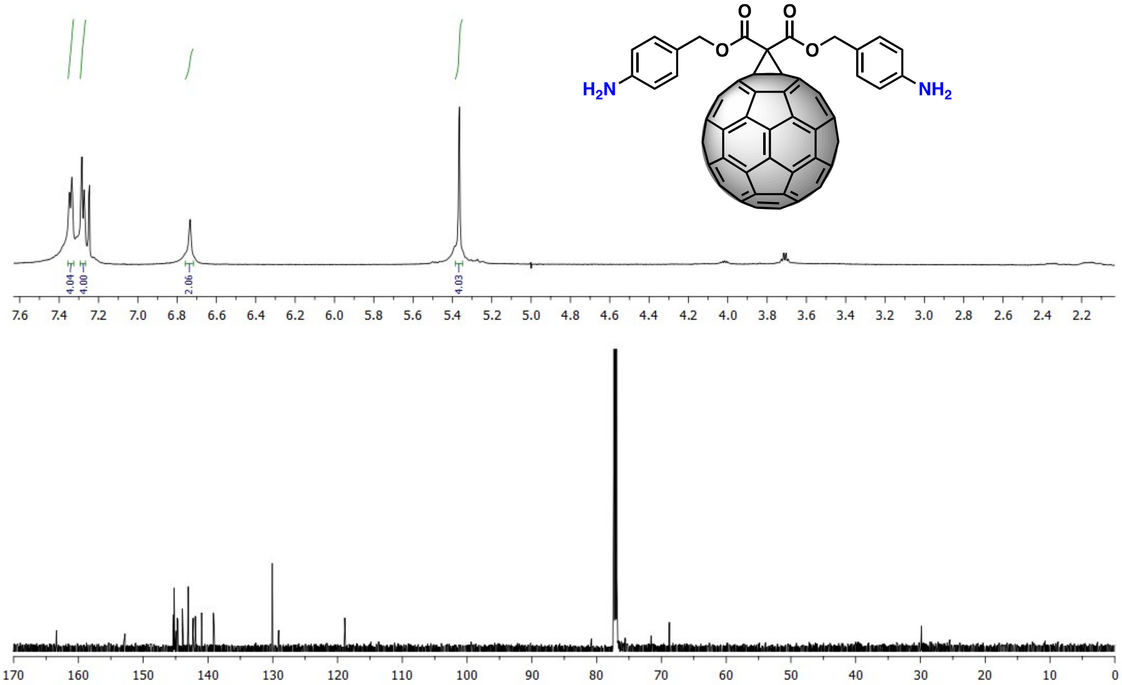


g) Compound 5





h) BAn-C_{60}



Photovoltaic Characterization

Figure S1: Electron mobility of different fullerene derivatives

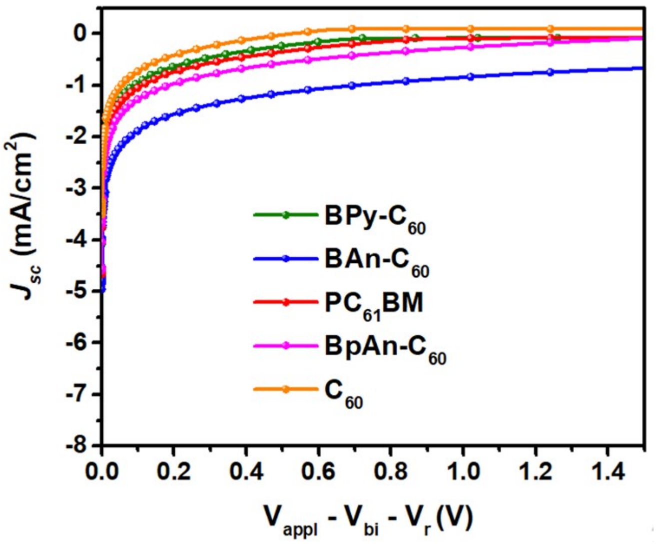


Table S1: Electron mobility values of different fullerene derivatives

Compound	**Electron mobility ($cm^2\ V^{-1}\ s^{-1}$)**
$PC_{61}BM$	5.74×10^{-4}
C_{60}	6.21×10^{-4}
BPy-C_{60}	1.22×10^{-4}
BAn-C_{60}	9.29×10^{-5}
BpAn-C_{60}	1.15×10^{-4}

Figure S2: Conductivity of different fullerene derivatives

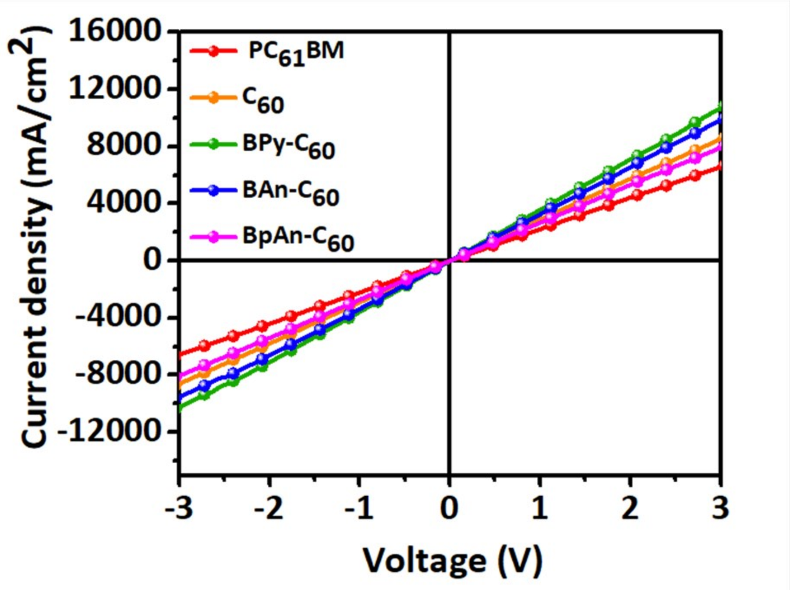


Table S2: Conductivity Values of different fullerene derivatives

Compound	**Conductivity (S•cm^{-1})**
$PC_{61}BM$	1.12×10^{-4}
C_{60}	5.86×10^{-3}
BPy-C_{60}	6.32×10^{-3}
BAn-C_{60}	4.86×10^{-3}
BpAn-C_{60}	5.24×10^{-3}

Figure S3: Statistical Analysis of the photovoltaic parameters

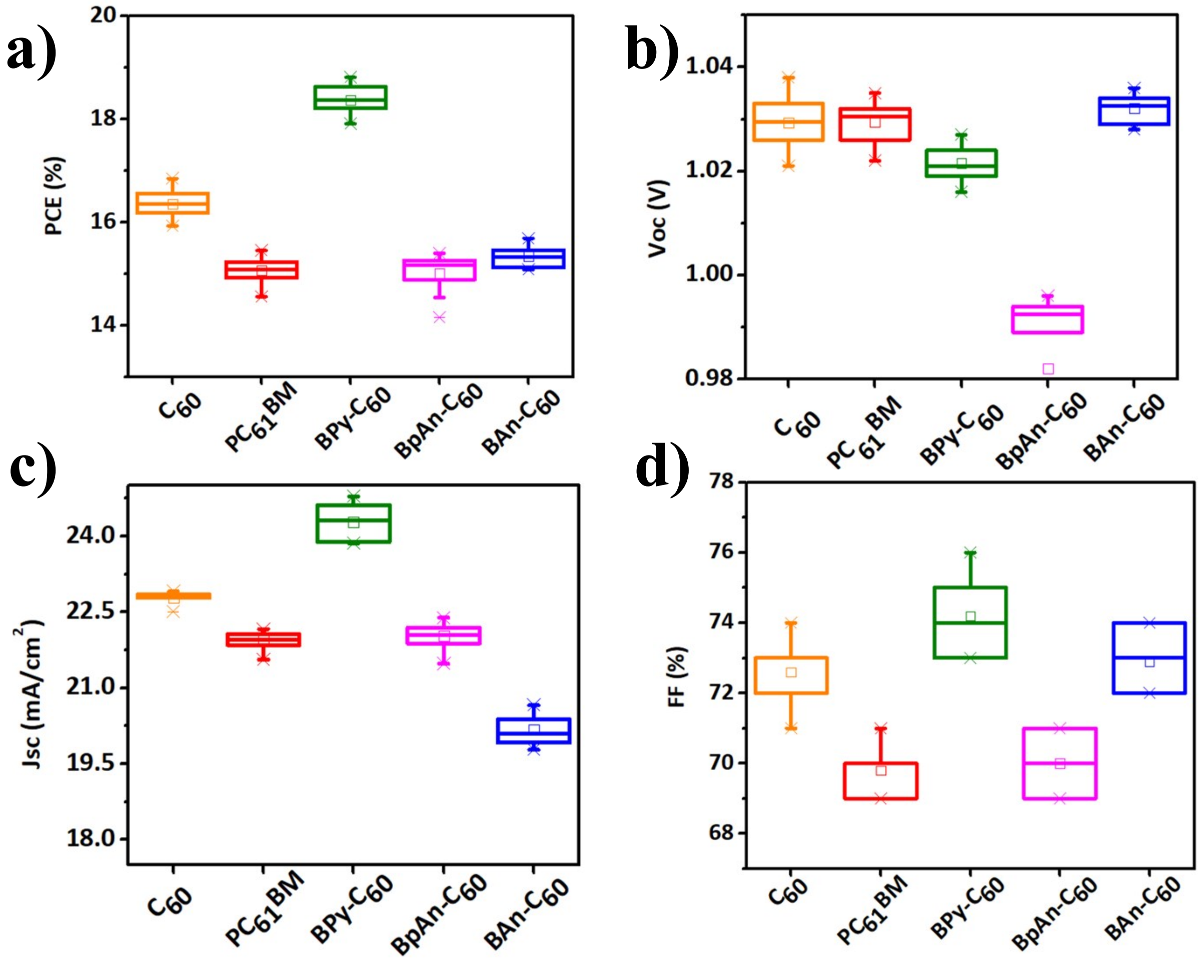


Figure S4: Stability Studies for devices with BPy-C_{60} and C_{60}