Electronic Supplementary Material (ESI) for New Journal of Chemistry.

New thiophene-based C_{60} fullerene derivatives as efficient electron transporting materials for perovskite solar cells

Edison Castro,[a†*] Olivia Fernandez-Delgado,[a†] Funda Arslan,[a] Gerardo Zavala,[a] Tingyuan Yang,[a] Sairaman Seetharaman,[b] Francis D'Souza,[b] and Luis Echegoyen*[a]

[a] Department of Chemistry, University of Texas at El Paso, 500 West University Avenue, El Paso, TX 79968, United States

[b] Department of Chemistry, University of North Texas Denton, TX 76203-5017, United States

*E-mail: eacastroportillo@utep.edu

*E-mail: echegoyen@utep.edu

Device Characterization

Current-Voltage (*J-V*) characteristics of photovoltaic cells were tested using a Keithley 2420 source meter under a Photo Emission Tech SS100 Solar Simulator, and the light intensity was calibrated by a standard Si solar cell. External quantum efficiency (EQE) was measured using a Bentham (from Bentham Instruments Ltd) measurement system. The light intensity was calibrated using a single-crystal Si photovoltaic cell as reference. The *J-V* and EQE measurements were obtained in air. The scanning electron microscopy (SEM) images were collected using a ZEISS Sigma FE-SEM, where the electron beam was accelerated in the range of 500 V to 30 kV. Film thicknesses were measured using a KLA Tencor profilometer. The steady-state PL spectra were recorded on a Horiba Yvon Nanolog spectrometer coupled with a time-correlated single photon counting (TCSPC) with nanoLED excitation sources for time-resolved emission measurements.

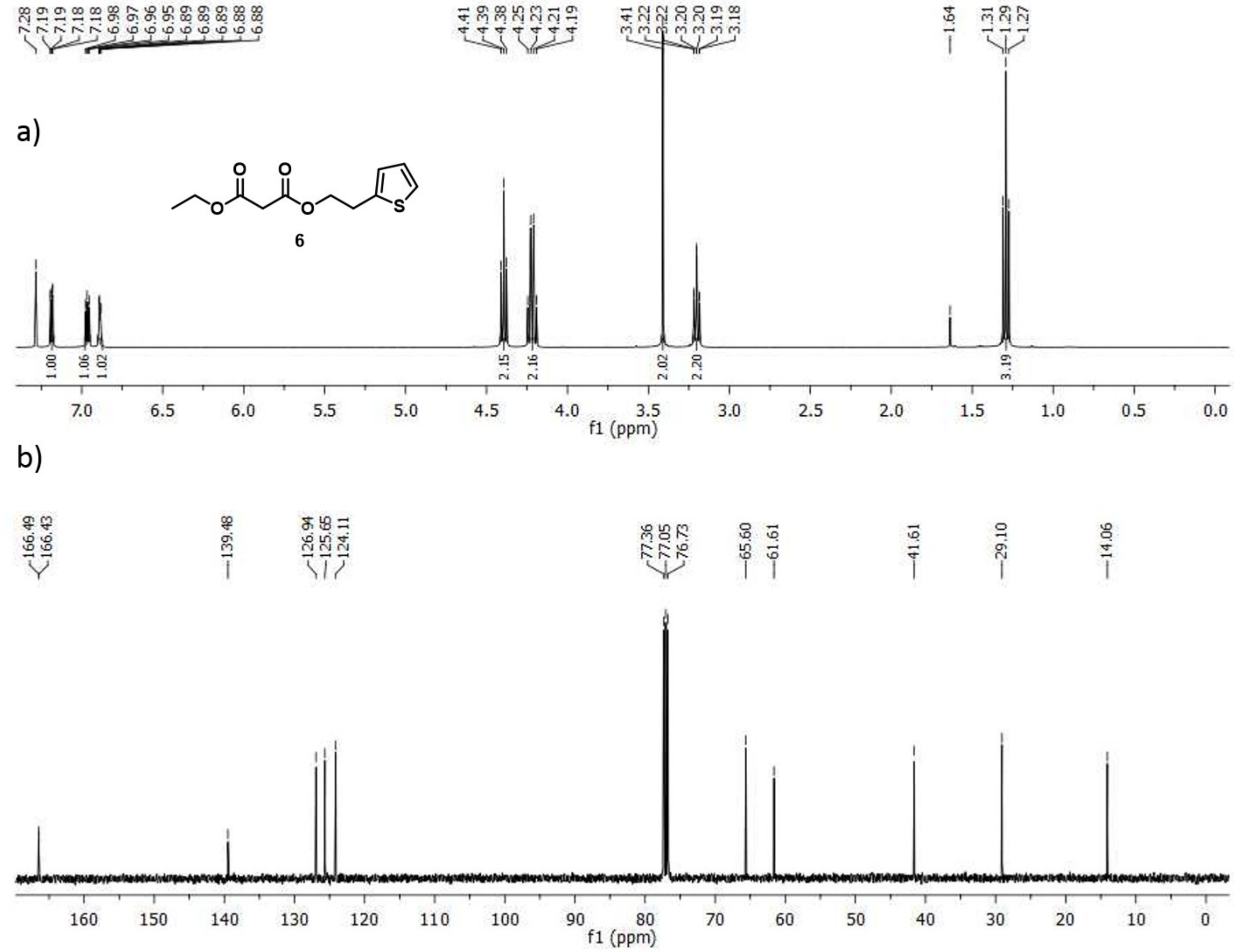

Figure S1: a) ^{1}H and b) ^{13}C NMR spectra of compound **6**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, 1H), 6.97 (dd, 1H), 6.89-6.88 (m, 1H), 4.39 (t, 2H), 4.22 (q, 2H), 3.41 (s, 2H), 3.20 (t, 2H), 1.29 (t, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 166.4, 139.5, 126.9, 125.7, 124.1, 65.6, 61.6, 41.6, 29.1, 14.1 ppm.

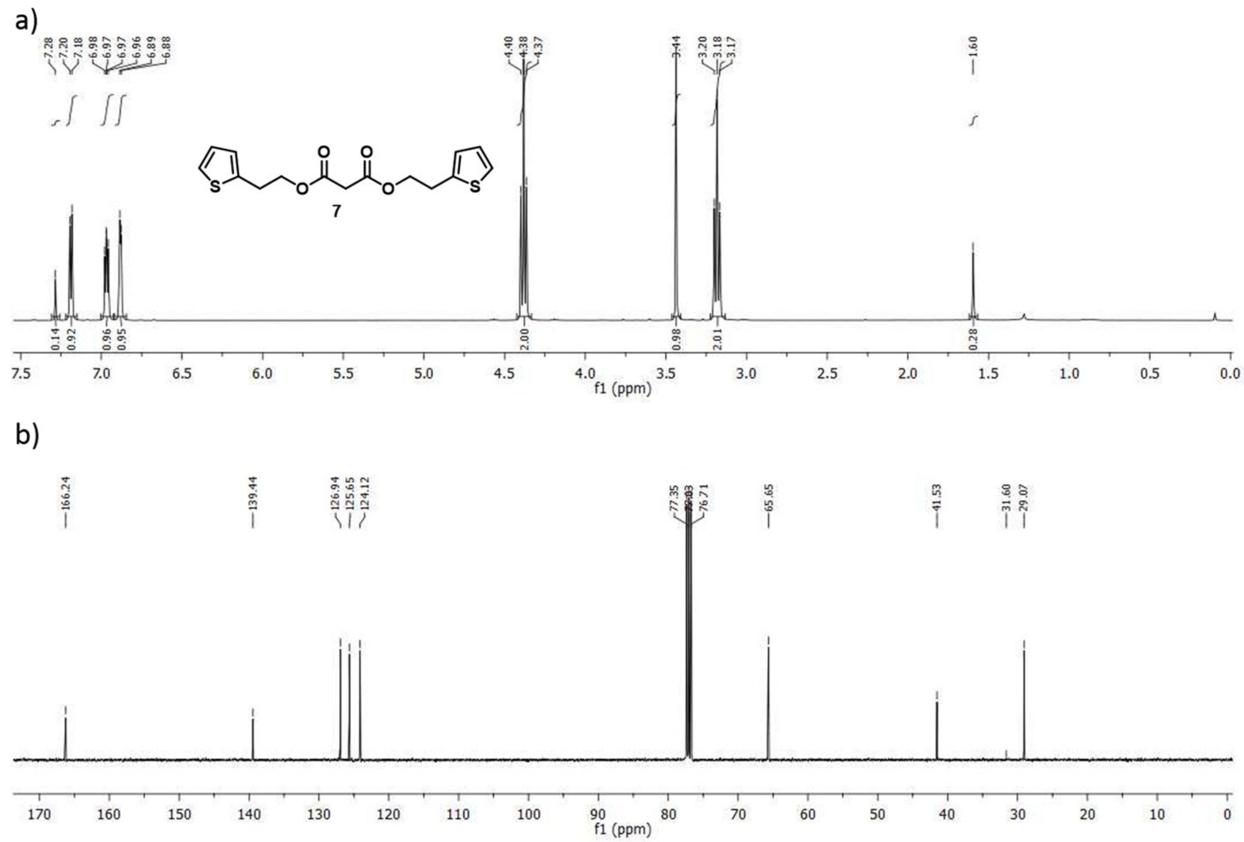

Figure S2: a) ^{1}H and b) ^{13}C NMR spectra of compound **7**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, 2H), 6.97 (t, 2H), 6.89 (d, 2H), 4.38 (t, 4H), 3.44 (s, 2H), 3.18 (t, 4H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 139.5, 127.3, 125.7, 124.1, 65.7, 41.5, 29.1 ppm.

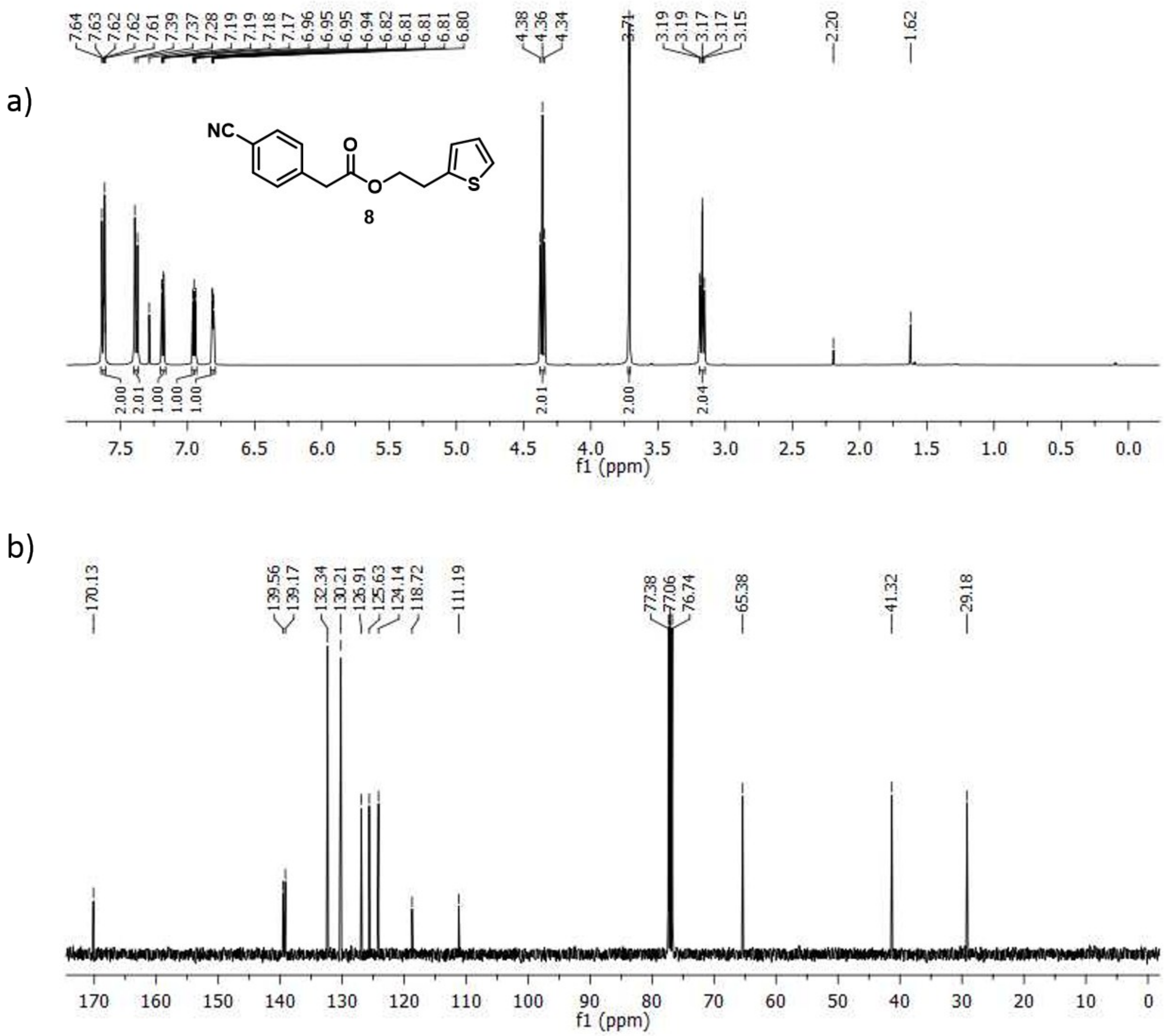

Figure S3: a) ^{1}H and b) ^{13}C NMR spectra of compound **8**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.61 (m, 2H), 7.38 (d, 2H), 7.18 (dd, 1H), 6.95 (dd, 1H), 6.81- 6.80 (m, 1H), 4.36 (t, 2H), 3.71 (s, 1H), 3.17 (t, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 139.6, 139.2, 132.3, 130.2, 126.9, 125.6, 124.1, 118.7, 111.2, 65.4, 41.3, 29.2 ppm.

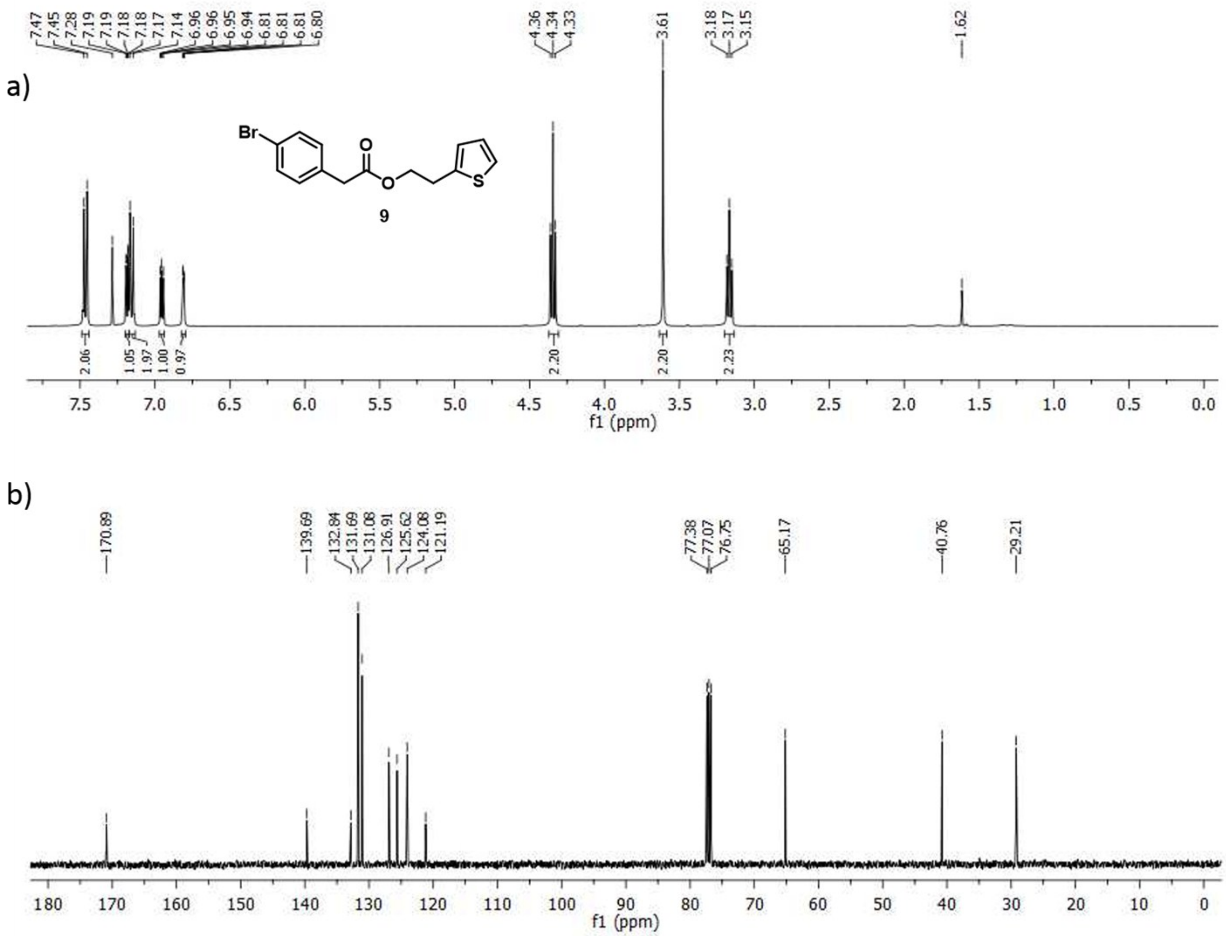

Figure S4: a) ^{1}H and b) ^{13}C NMR spectra of compound **9**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, 2H), 7.19 (dd, 1H), 7.16 (d, 2H), 6.95 (dd, 1H), 6.81 (dd, 1H), 4.34 (t, 2H), 3.61 (s, 2H), 3.16 (t, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 139.7, 132.8, 131.7, 131.1, 126.9, 125.6, 124.1, 121.2, 65.2, 40.7, 29.2 ppm.

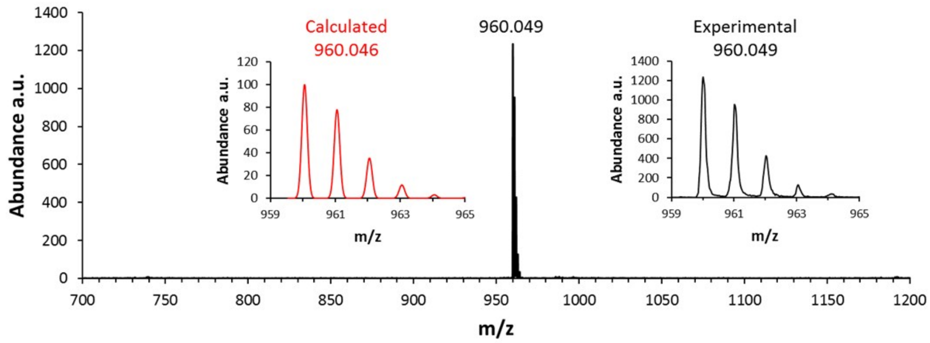

Figure S5: MALDI-TOF-MS spectrum of compound **10.**

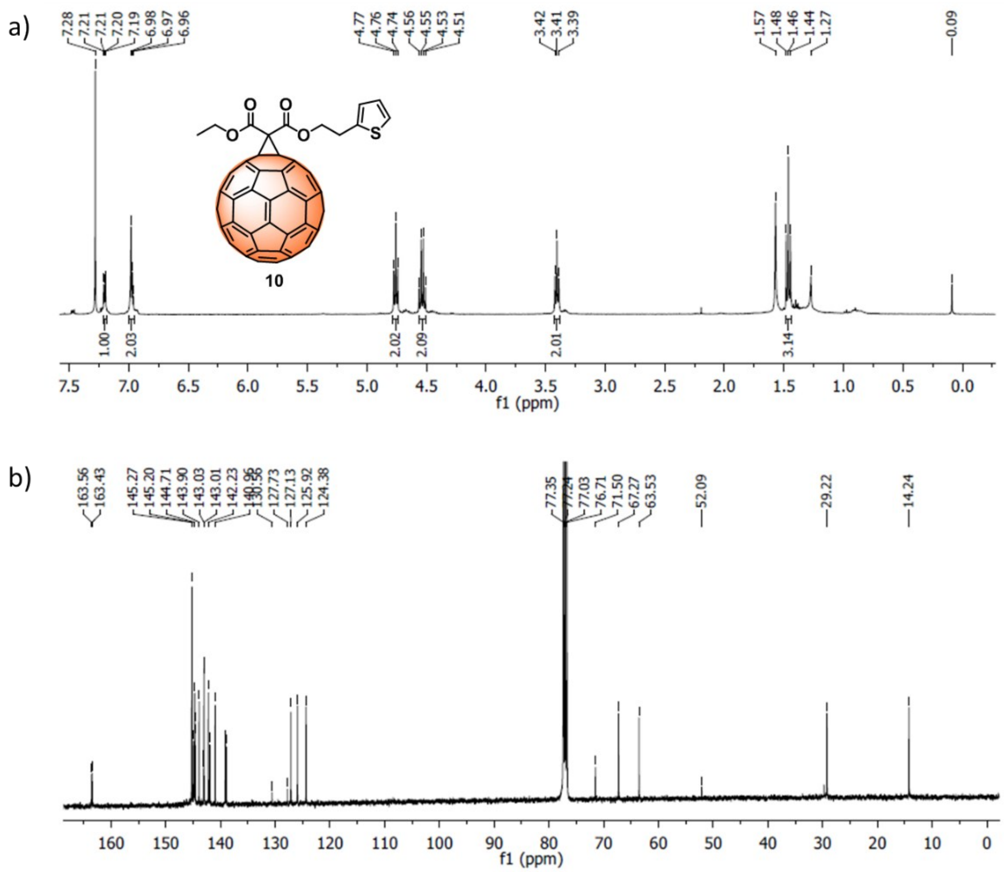

Figure S6: a) ^{1}H and b) ^{13}C NMR spectra of compound **10.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, 1H), 6.98-6.96 (m, 2H), 4.76 (t, 2H), 4.54 (q, 2H), 3.40 (t, 2H), 1.46 (t, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 163.4, 145.4, 145.3, 145.2, 144.9, 144.7, 144.6, 144.6, 143.9, 143.2, 143.1, 143.0, 143.0, 142.2, 142.0, 141.9, 141.0, 139.1, 139.1, 138.9, 130.6, 127.7, 127.1, 125.9, 124.4, 77.2, 71.5, 67.3, 63.5, 52.1, 29.2, 14.2 ppm.

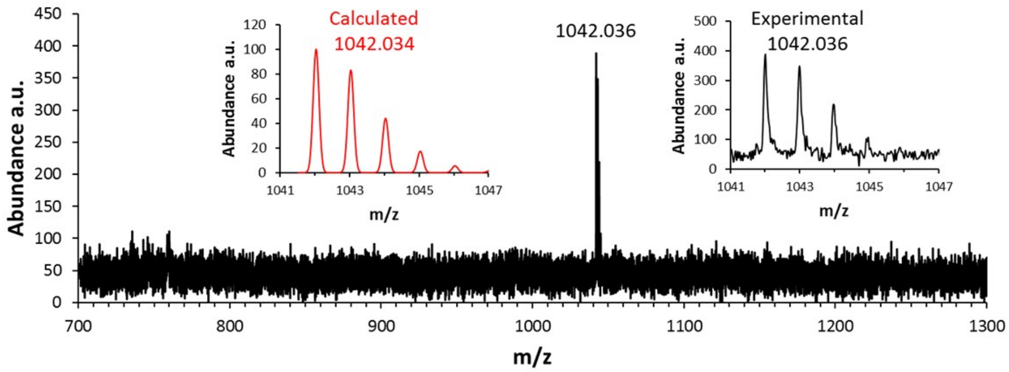

Figure S7: MALDI-TOF-MS spectrum of compound **11.**

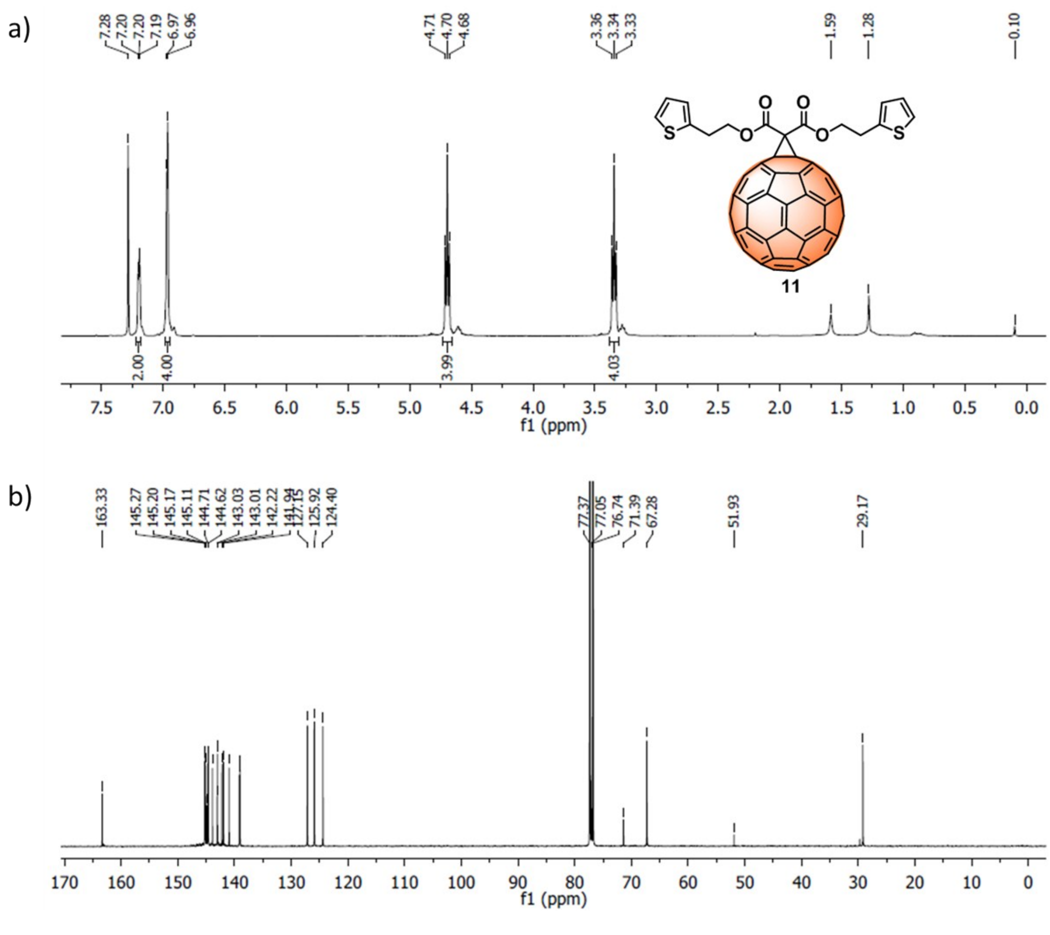

Figure S8: a) ^{1}H and b) ^{13}C NMR spectra of compound **11.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20- 7.19 (m, 2H), 6.97 (d, 4H), 4.70 (t, 4H), 3.34 (t, 4H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 145.3, 145.2, 145.1, 145.0, 144.9, 144.7, 144.6, 144.5, 143.9, 143.1, 143.0, 142.9, 142.2, 141.9, 140.9, 139.1, 139.0, 127.2, 125.9, 124.4, 71.4, 67.3, 51.9, 29.2 ppm.

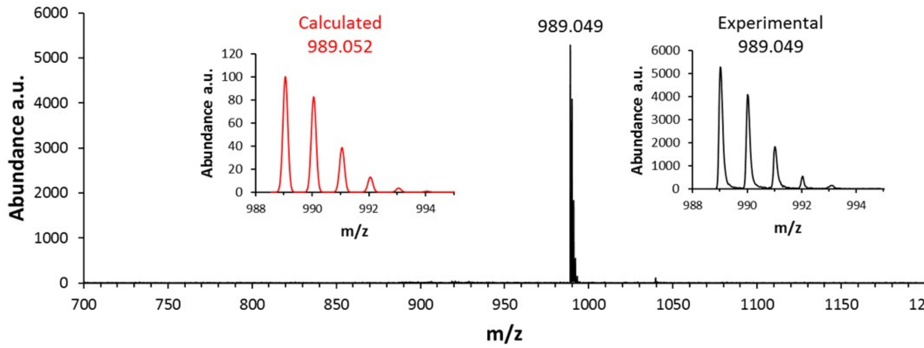

Figure S9: MALDI-TOF-MS spectrum of compound **11.**

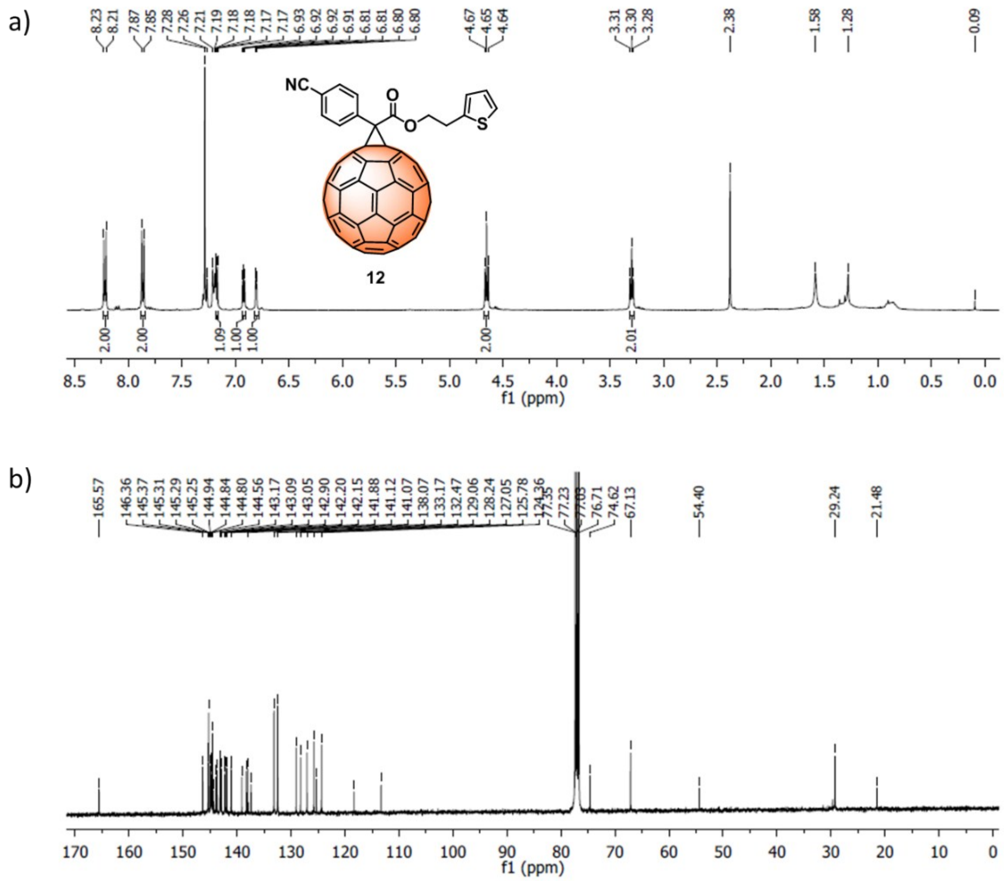

Figure S10: a) ^{1}H and b) ^{13}C NMR spectra of compound **12.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, 2H), 7.86 (dd, 2H), 7.18 (dd, 1H), 6.92 (dd, 1H), 6.81 (dd, 1H), 4.65 (t, 2H), 3.30 (t, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 146.4, 145.4, 145.3, 145.3, 145.2, 144.9, 144.8, 144.8, 144.7, 144.6, 144.5, 144.4, 143.9, 143.7, 143.2, 143.1, 143.0, 142.9, 142.3, 142.2, 142.1, 141.9, 141.1, 141.0, 139.1, 138.3, 138.1, 137.4, 133.2, 132.5, 129.1, 128.2, 127.1, 125.8, 125.31, 124.4, 118.3, 113.3, 77.2, 74.6, 67.1, 54.4, 29.2, 21.5 ppm.

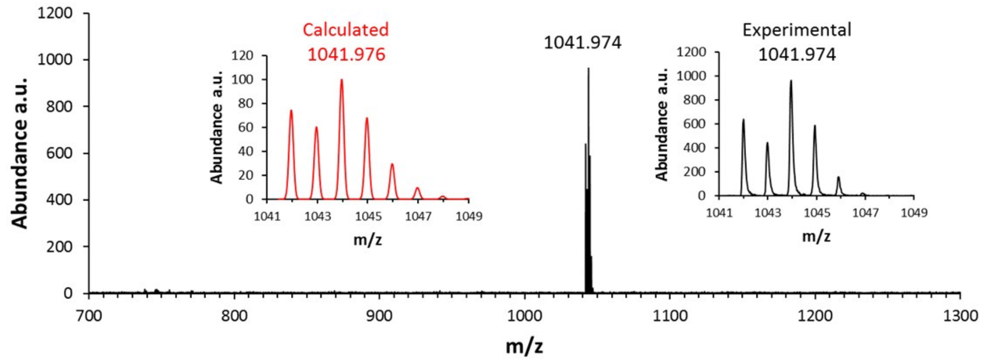

Figure S11: MALDI-TOF-MS spectrum of compound **13.**

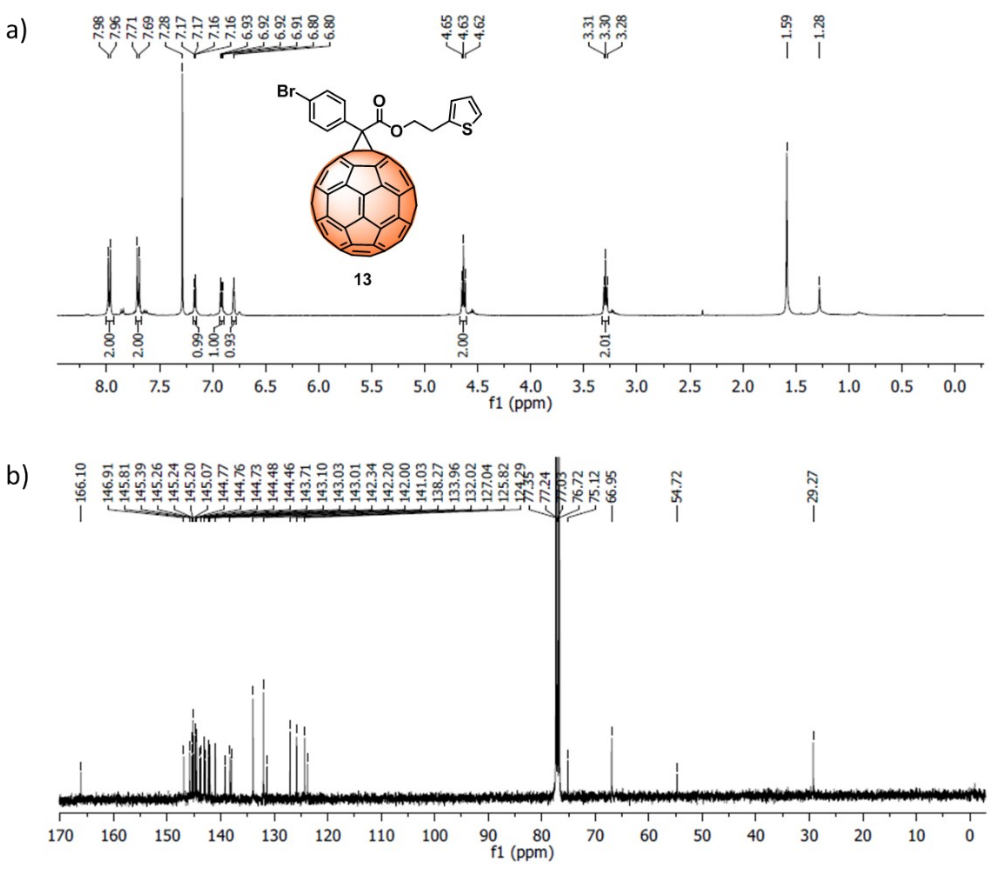

Figure S12: a) ^{1}H and b) ^{13}C NMR spectra of compound **13.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, 2H) 7.70 (d, 2H), 7.17 (dd, 1H) 6.92 (dd, 1H) 6.81 (d, 1H), 4.63 (t, 2H), 3.29 (t, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 146.9, 145.8, 145.4, 145.3, 145.2, 145.2, 145.1, 144.8, 144.7, 144.6, 144.5, 144.4, 144.3, 143.9, 143.7, 143.1, 143.0, 143.0, 142.9, 142.9, 142.3, 142.2, 142.1, 142.0, 141.0, 141.0, 139.2, 138.3, 138.0, 134.0, 132.0, 131.4, 127.0, 125.8, 124.3, 123.8, 77.2, 75.1, 66.9, 54.7, 29.3 ppm.

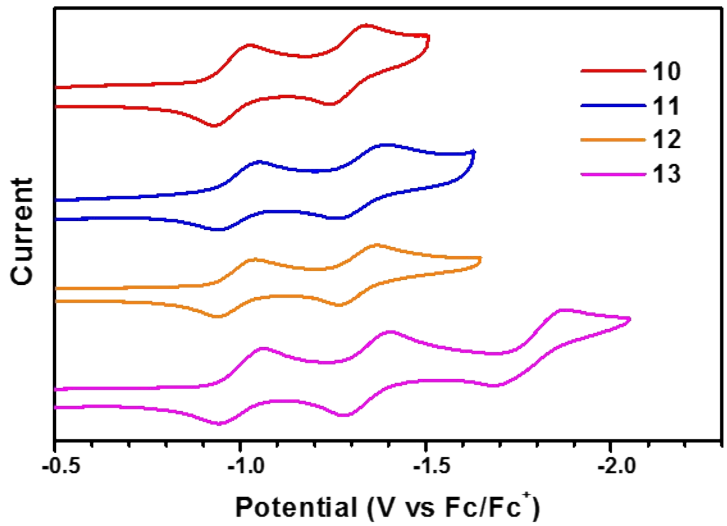

Figure S13: Cyclic voltammetry of compounds **10-13.**

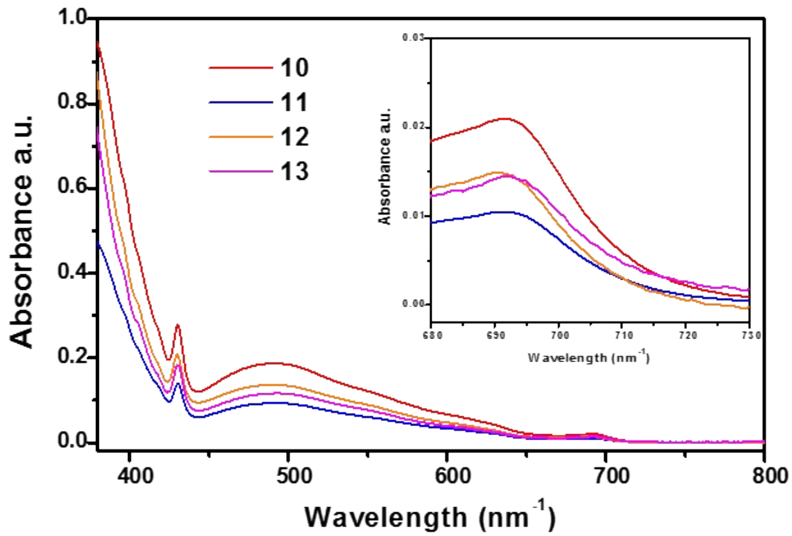

Figure S14: UV-Vis spectra of compounds **10-13.**

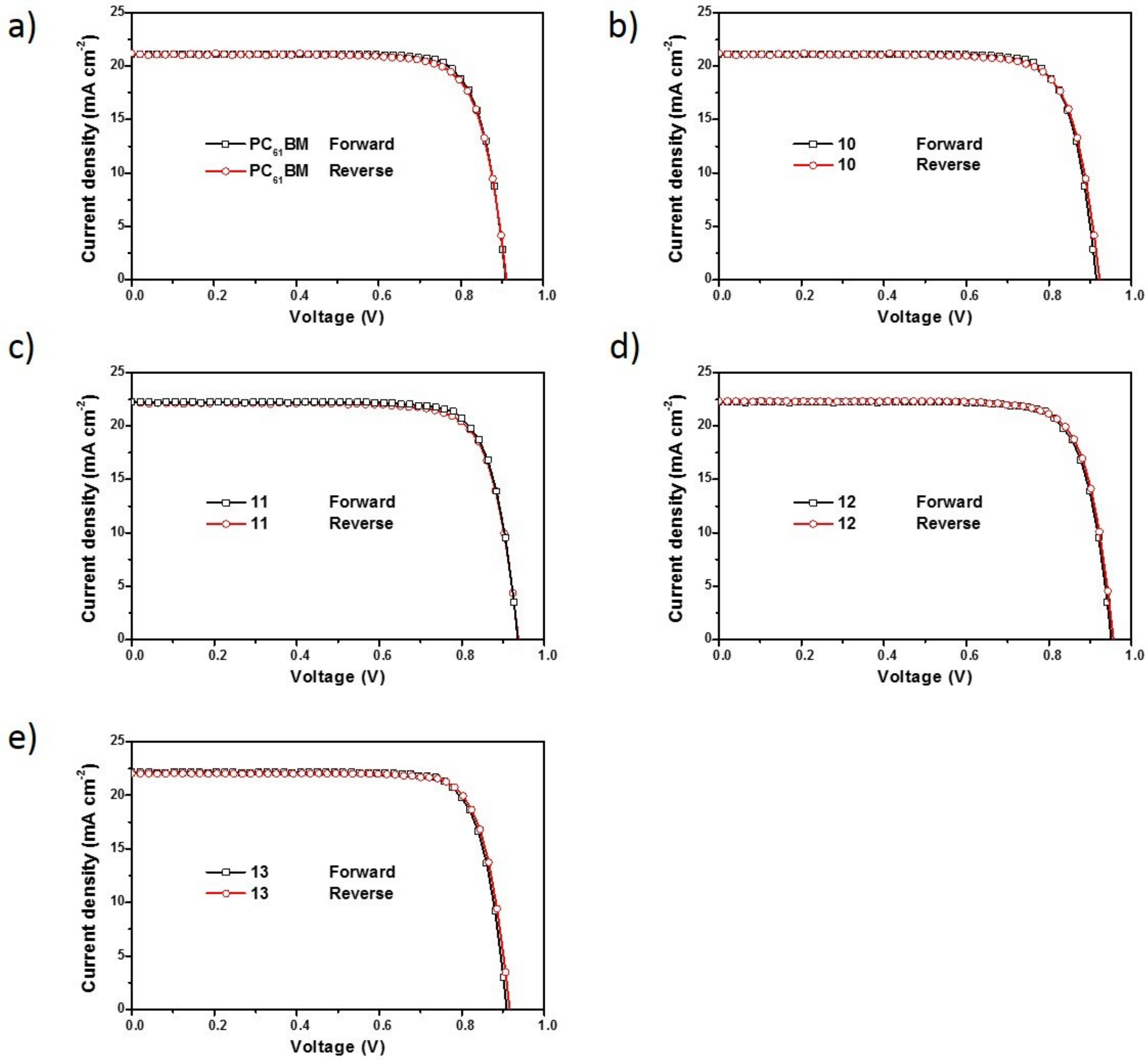

Figure S15: Forward and reverse scans for a) $PC_{61}BM$, b) compound **10,** c) compound **11,** d) compound **12,** e) compound **13.**

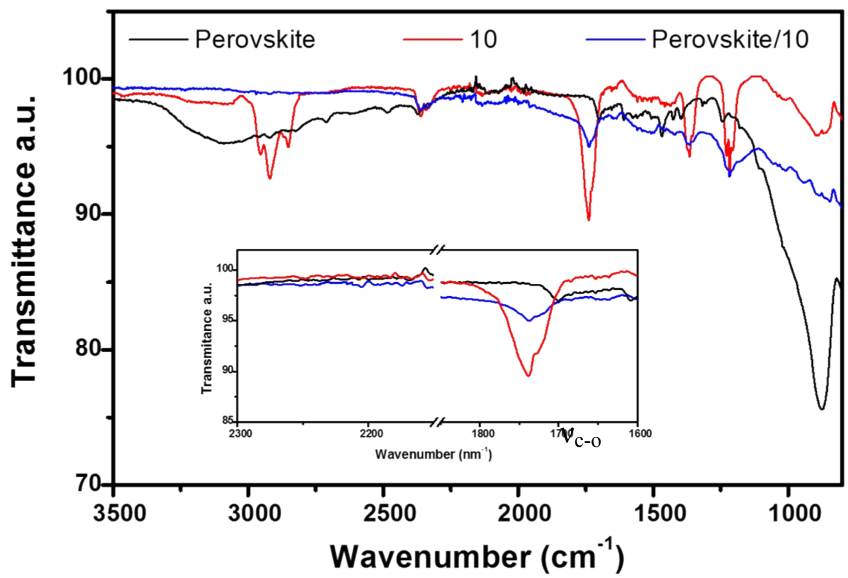

Figure S16: FTIR spectrum of compound **10.**

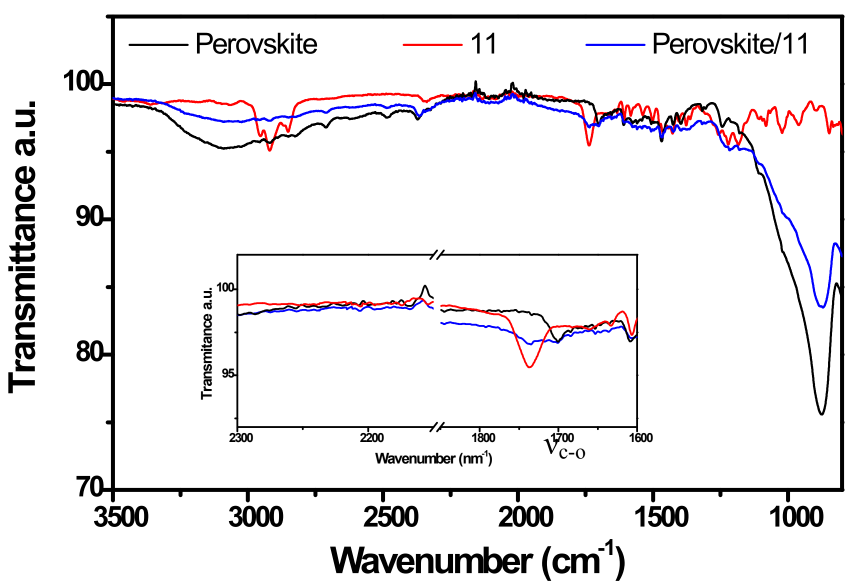

Figure S17: FTIR spectrum of compound **11.**

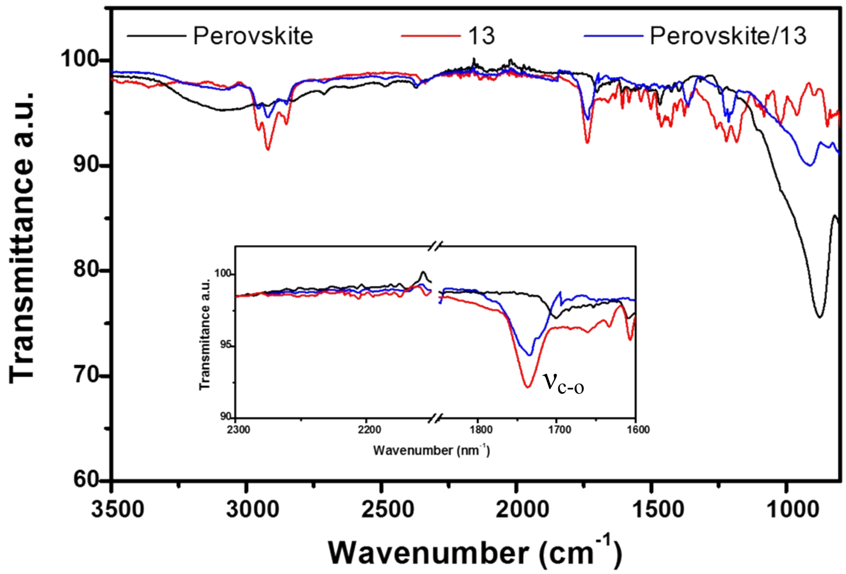

Figure S18: FTIR spectrum of compound **13.**

Dielectric constant measurement

We followed the method reported by Hummelen *et al*.[1] Dielectric constants were obtained by spectral impedance measurements using the following architecture: ITO/PEDOT:PSS/fullerene/Al. The capacitance was determined by filling the data to the equivalent circuit (Figure S19) for fabricated capacitors.

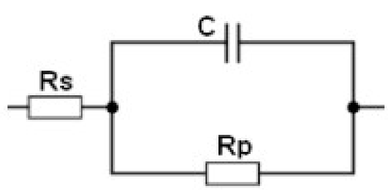

Figure S19. Equivalent circuit to fit the data, with capacitance (C), parallel resistance (Rp) and serial resistance (Rs).

The dielectric constant was determined using the equation S1:

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d} \qquad \text{(S1)}$$

where A is the capacitor's area (m^2), d is the thickness of the fullerene film (m) and ε_0 is the permittivity of vacuum (8.85×10^{-12} F/m).

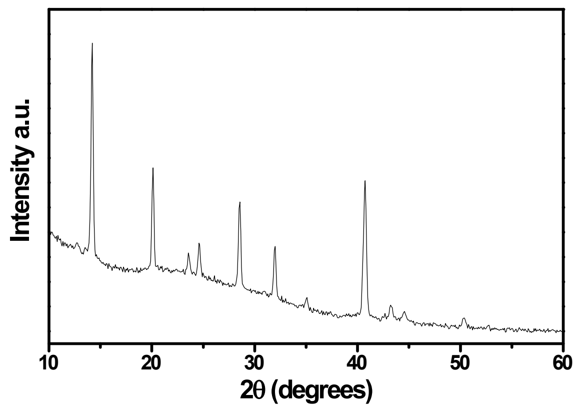

Figure S20. XRD of the perovskite film.

References

1. F. Jahani, S. Torabi, R. C. Chiechi, L. J. A. Koster and J. C. Hummelen. *Chem. Commun.* 2014, **50**, 10645-10647.