

## Supporting Information

### Impact of Fullerene Derivative Isomeric Purity on the Performance of Inverted Planar Perovskite Solar Cells

*Edison Castro, Gerardo Zavala, Sairaman Seetharaman, Francis D'Souza, and Luis Echegoyen\**

E. Castro, E. G. Zavala, Prof. L. Echegoyen

Department of Chemistry

University of Texas at El Paso

El Paso, Texas, 79968, United States

E-mail: [echegoyen@utep.edu](mailto:echegoyen@utep.edu)

S. Seetharaman, Prof. F. D'Souza

Department of Chemistry

University of North Texas

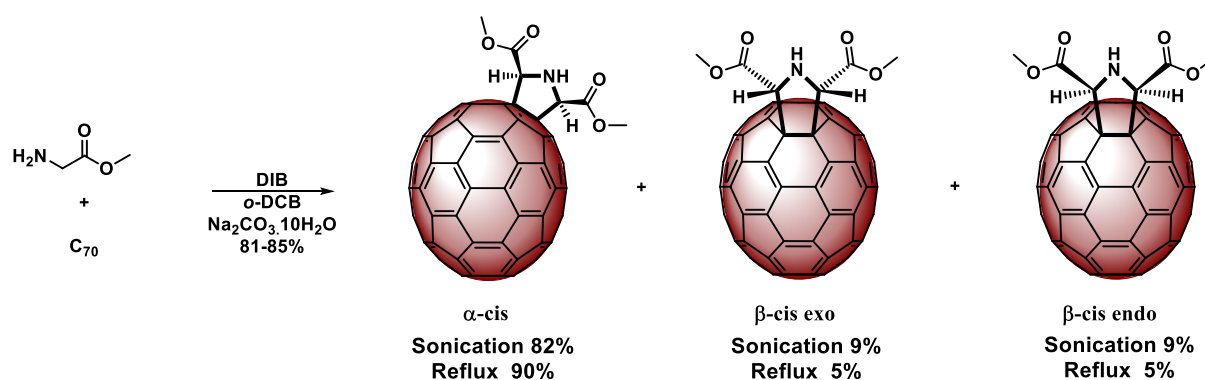
Denton, TX 76203-5017, United States.

### General Methodology

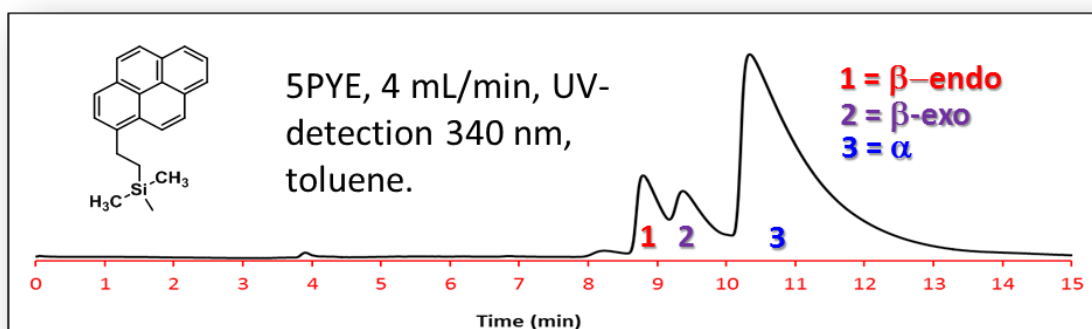
All chemicals were reagent grade, purchased from Sigma Aldrich. Silica gel (Redisep silica, 40-60  $\mu$ , 60  $\text{\AA}$ ) was used to separate the products from the pristine fullerene. HPLC experiments were performed on an LC-9130NEXT apparatus (Japan Analytical Industry Co. Ltd.) monitored using a UV detector at 320 nm, and toluene as eluent. MALDI-TOF mass spectrometric measurements were conducted on a Bruker Microflex LRF mass spectrometer on reflector positive mode. The NMR spectra were recorded using a JEOL 600 MHz spectrometer. The UV/Vis-NIR spectra were taken using a Cary 5000 UV/Vis-NIR spectrophotometer using chloroform solutions. Cyclic voltammetry (CV) experiments were carried out under an Argon atmosphere at room temperature using a CH Instrument Potentiostat. Scan rate for CV experiments was 100 mV/s. A one compartment cell with a standard three-electrode set up was

used, consisting of a 1 mm diameter glassy carbon disk as the working electrode, a platinum wire as the counter electrode and a silver wire as the pseudo-reference electrode, in a solution of anhydrous *o*-DCB containing 0.05 M  $n\text{-Bu}_4\text{NPF}_6$ . Ferrocene was added to the solution at the end of each experiment as an internal standard.

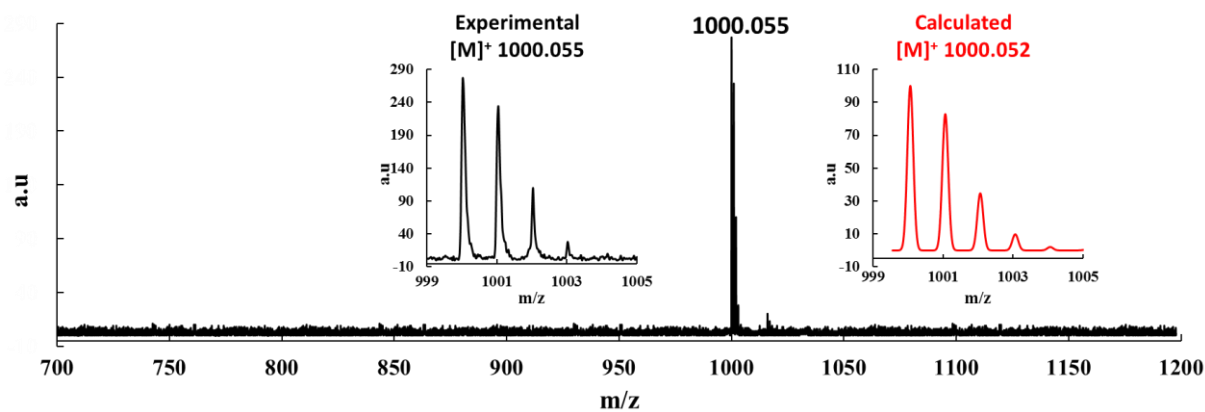
## Experimental Section



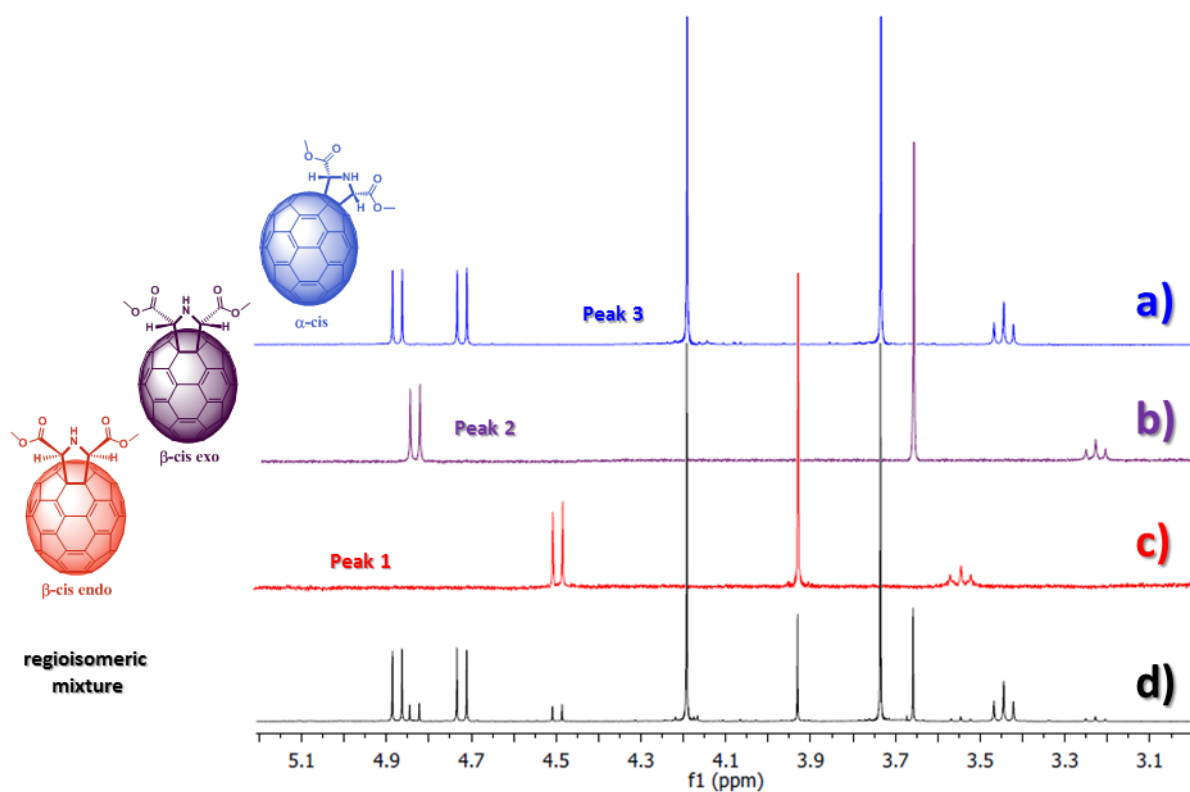
**Scheme S1.** Synthesis of  $\text{DMEC}_{70}$  fullerene derivatives. The structures of the chiral  $\alpha$ -type isomer (left) and the two possible achiral  $\beta$ -type isomers (right). The percentage was calculated from 3 independent reactions.



**Figure S1.** HPLC chromatogram of the  $\text{C}_{70}$  mono-adducts regioisomeric mixture.



**Figure S2.** MALDI-TOF spectrum of DMEC<sub>70</sub> using 1,8,9-trihydroxyanthracene (THA) as matrix C<sub>70</sub>.

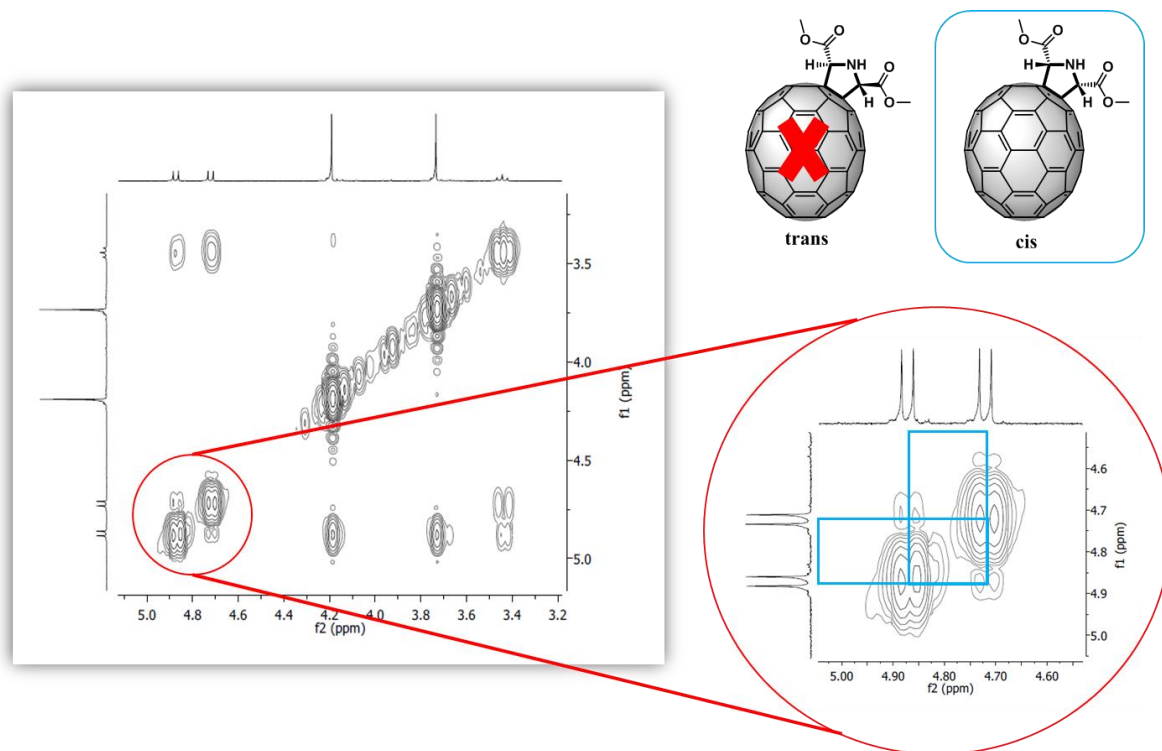


**Figure S3.** <sup>1</sup>H-NMR of the DMEC<sub>70</sub> fullerene derivatives, before and after HPLC purification (CDCl<sub>3</sub>, 298 K, 600 MHz). a)  $\alpha$ -cis b)  $\beta$ -cis exo c)  $\beta$ -cis endo d) regioisomeric mixture.

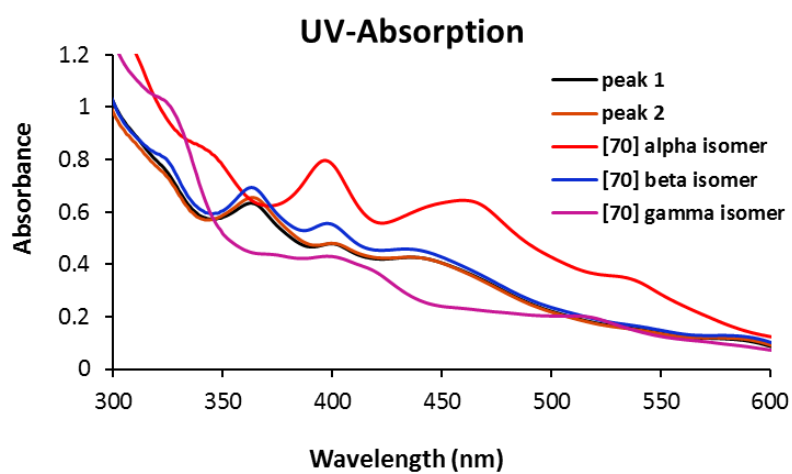
$\alpha$ -DMEC<sub>70</sub> <sup>1</sup>H NMR (600 MHz; CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm) 4.89 (*d*, *J* = 13.7 Hz, 1 H,  $\alpha$ -CH), 4.73 (*d*, *J* = 13.8 Hz, 1 H,  $\alpha$ -CH), 4.20 (*s*, 3 H,  $\alpha$ -CH<sub>3</sub>), 3.75 (*s*, 3 H,  $\alpha$ -CH<sub>3</sub>), 3.46 (*t*, *J* = 13.8 Hz, 1 H,  $\alpha$ -NH).

**$\beta$ -exo-DMEC<sub>70</sub>** <sup>1</sup>H NMR (600 MHz; CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm) 4.84 (*d*, *J* = 13.7 Hz, 2 H,  $\beta$ -CH), 3.67 (*s*, 6 H,  $\beta$ -CH<sub>3</sub>), 3.24 (*t*, *J* = 13.7 Hz, 1 H,  $\beta$ -NH).

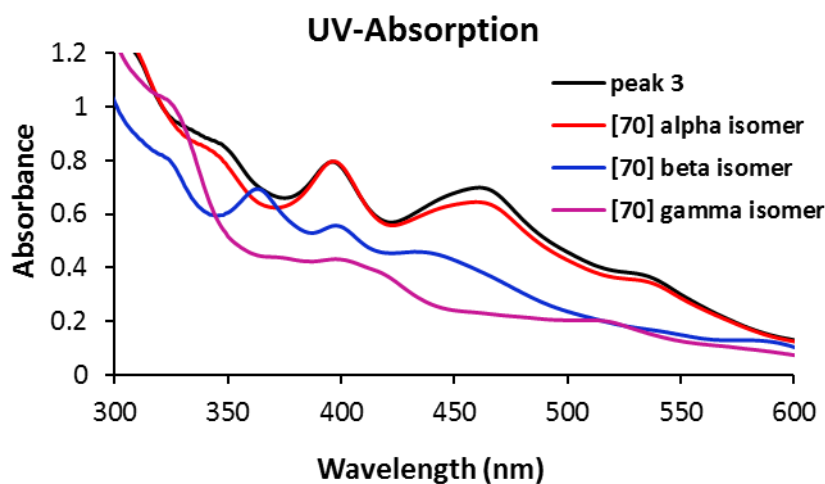
**$\beta$ -endo-DMEC<sub>70</sub>** <sup>1</sup>H NMR (600 MHz; CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm) 4.51 (*d*, *J* = 13.7 Hz, 2 H,  $\beta$ -CH), 3.94 (*s*, 6 H,  $\beta$ -CH<sub>3</sub>), (*t*, *J* = 13.7 Hz, 1 H,  $\beta$ -NH).



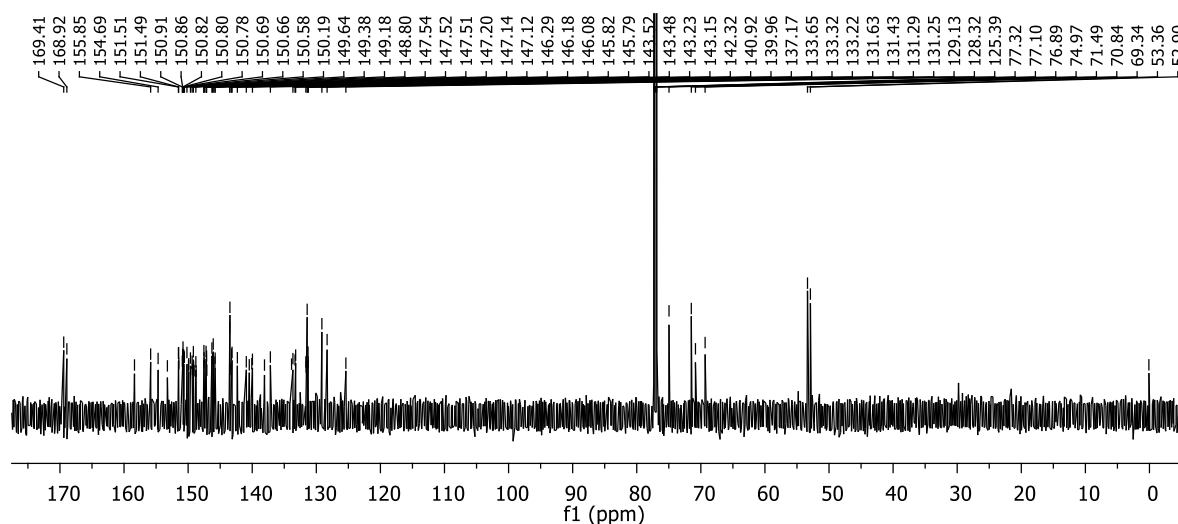
**Figure S4.** NOESY of the  $\alpha$ -DMEC<sub>70</sub> isomer.



**Figure S5.** UV-Vis spectra of  $\beta$ -endo-DMEC<sub>70</sub> (peak 1),  $\beta$ -exo-DMEC<sub>70</sub> (peak 2),  $\alpha$ -pyrrolidine-C<sub>70</sub>,  $\beta$ -pyrrolidine-C<sub>70</sub> and  $\gamma$ -pyrrolidine-C<sub>70</sub> in chloroform.



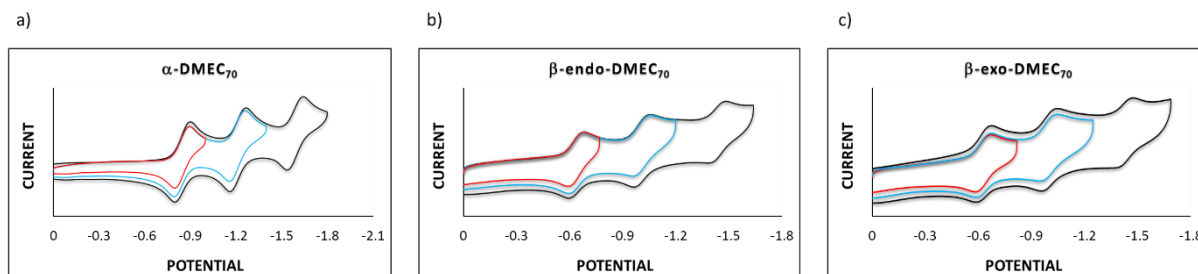
**Figure S6.** UV-Vis spectra of  $\alpha$ -exo-DMEC<sub>70</sub> (peak 3),  $\alpha$ -pyrrolidine-C<sub>70</sub>,  $\beta$ -pyrrolidine-C<sub>70</sub> and  $\gamma$ -pyrrolidine-C<sub>70</sub> in chloroform.



**Figure S7.** <sup>13</sup>C NMR (150 MHz; CDCl<sub>3</sub>, 298 K) of  $\alpha$ -DMEC<sub>70</sub>.

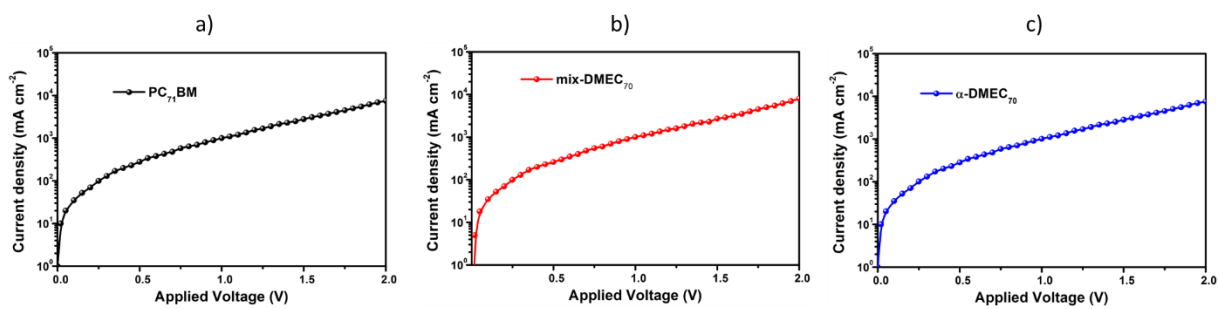
<sup>13</sup>C NMR (150 MHz; CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm) 169.4, 168.9, 158.4, 155.9, 154.7, 153.2, 151.5, 151.5, 151.5, 150.9, 150.9, 150.8, 150.8, 150.8, 150.8, 150.7, 150.7, 150.6, 150.2, 150.1, 149.9, 149.9,

149.6, 149.4, 149.3, 149.2, 149.1, 149.1, 149.1, 148.8, 148.8, 147.5, 147.5, 147.5, 147.2, 147.1, 147.1, 147.1, 147.0, 146.3, 146.2, 146.1, 146.0, 145.8, 145.8, 143.5, 143.5, 143.4, 143.3, 143.2, 143.2, 142.3, 140.9, 140.5, 140.1, 140.0, 138.1, 137.2, 133.9, 133.7, 133.3, 133.2, 131.6, 131.6, 131.4, 131.3, 131.3, 129.1, 128.3, 125.4, 75.0, 71.5, 70.8, 69.3, 53.4, 52.9.

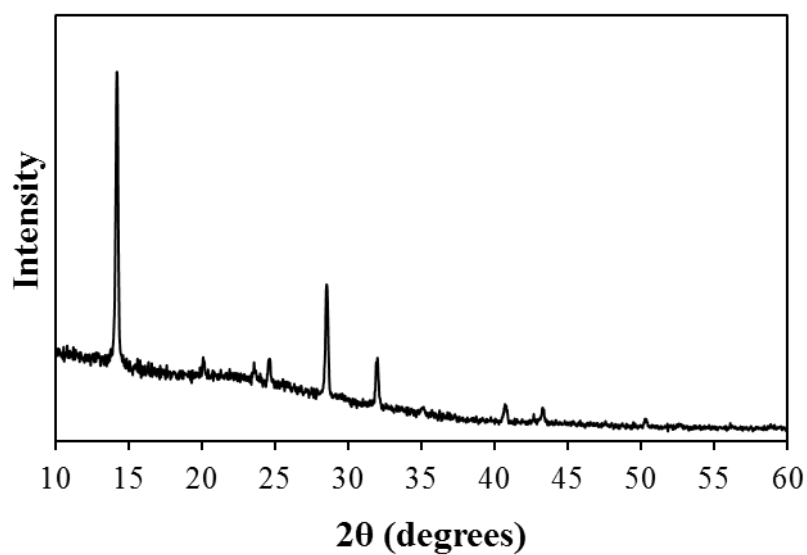


**Figure S8.** Cyclic voltammetry of a)  $\alpha$ -DMEC<sub>70</sub> b)  $\beta$ -endo-DMEC<sub>70</sub> and c)  $\beta$ -exo-DMEC<sub>70</sub> (*o*-DCB containing 0.05 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>; using the redox couple Fc/Fc<sup>+</sup> as internal reference).

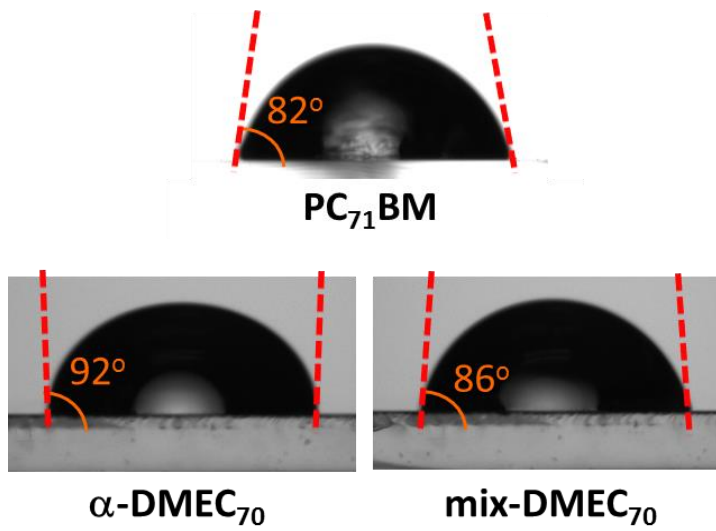
*Device characterization:* *J-V* characteristics of photovoltaic cells were tested using a Keithley 2420 source meter under a Photo Emission Tech SS100 Solar Simulator, and the light intensity was calibrated by a standard Si solar cell. EQEs were measured using a Bentham (from Bentham Instruments Ltd) measurement system. The light intensity was calibrated using a single-crystal Si photovoltaic cell as the reference. The *J-V* and EQE measurements were carried out in air. The 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 contact angles of water were determined using a Ramé-Hart model 250 goniometer using pure deionized water at room temperature at a constant volume of 5  $\mu$ L. A total of ten static measurements were analyzed and averaged for each ETL. The steady-state photoluminescence 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.



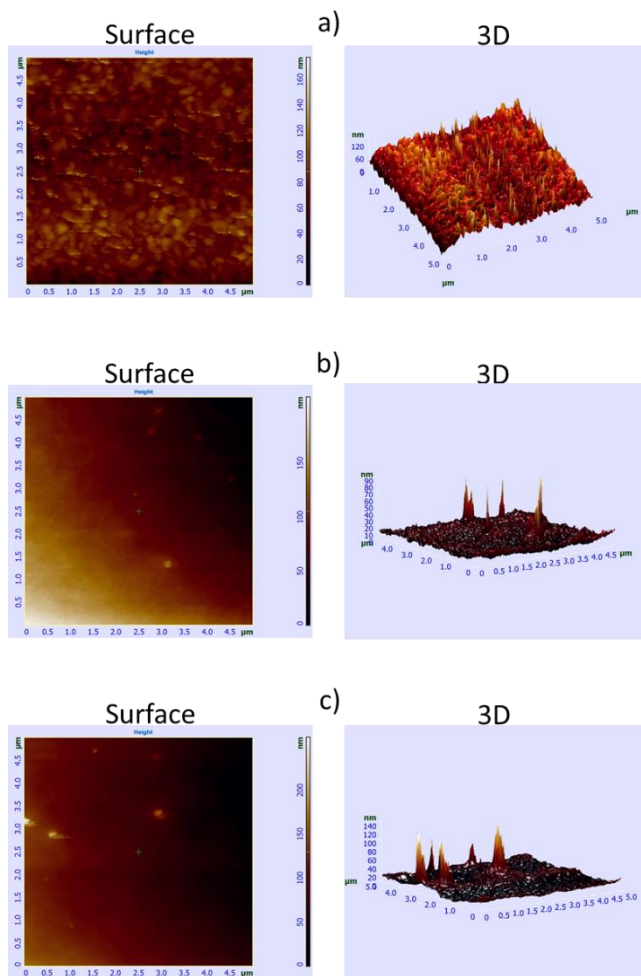
**Figure S9.** Measured space-charge limited  $J$ - $V$  characteristics of a) PC<sub>71</sub>BM, b) mix-DMEC<sub>70</sub> and c)  $\alpha$ -DMEC<sub>70</sub> for electron only devices with ITO/Al/fullerene/Al structure.



**Figure S10.** The XRD spectra of the perovskite films.



**Figure S11.** Images of the water droplet contact angles on the surfaces of PC<sub>71</sub>BM,  $\alpha$ -DMEC<sub>70</sub> and mix-DMEC<sub>70</sub> thin films.



**Figure S12.** AFM Images of a) perovskite layer, b) mix-DMEC<sub>70</sub> deposited on top of the perovskite layer and d)  $\alpha$ -DMEC<sub>70</sub> deposited on top of the perovskite layer.