Supporting Information

#### Effective Interfacial Layer to Enhance Efficiency of Polymer Solar Cells via Solution-Processed Fullerene-Surfactants

Chang-Zhi Li,<sup>a</sup> Chu-Chen Chueh, <sup>a</sup> Hin-Lap Yip,<sup>a,b</sup> Kevin M. O'Malley,<sup>c</sup> Wen-Chang Chen<sup>d</sup> and Alex K.-Y. Jen<sup>a, b, c,</sup> \*

Department of Materials Science and Engineering<sup>a</sup>, Advanced Materials for Energy Institute<sup>b</sup>, and Department of Chemistry<sup>c</sup>, University of Washington, Seattle, Washington 98195, Department of Chemical Engineering and Institute of Polymer Science and Engineering, National Taiwan University, Taipei 106, Taiwan.<sup>d</sup>

E-mail: ajen@u.washington.edu

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# **1. Synthetic Procedures**

General. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk technique. All <sup>1</sup>H (500 MHz) and <sup>13</sup>C (125 MHz) spectra were recorded on Bruker AV500 spectrometers. Spectra were reported in parts per million from internal tetramethylsilane ( $\delta$  0.00 ppm) or residual protons of the deuterated solvent for <sup>1</sup>H NMR and from solvent carbon (e.g.  $\delta$  77.00 ppm for chloroform) for <sup>13</sup>C NMR. The Matrix for MALDI-TOF-MS used 2:1 mixture of alpha-cyano-4-hydroxycinnamic acid (CHCA)/2,5-dihydroxybenzoic acid (DHB) in acetonitrile. Elemental analyses were performed by QTI, Whitehouse, NJ (www.gtionline.com). AFM images under tapping mode were taken on a Veeco multimode AFM with a Nanoscope III controller. 2,3,4-tris(2-(2methoxyethoxy)ethoxy)benzaldehyde and fulleropyrrolidines were synthesized according to literature methods.<sup>1</sup> C<sub>60</sub> was purchased from American Dye Source. Unless otherwise noted, materials were purchased from Aldrich Inc., and used after appropriate purification.



Synthesis of Fulleropyrrolidiums A solution of  $C_{60}$  (300 mg, 0.35 mmol), 2,3,4-tris(2-(2-methoxy)ethoxy)benzaldehyde (478 mg, 1.04 mmol) and Sarcosinic

<sup>&</sup>lt;sup>1</sup>Ref. for synthesis of benzaldehyde, Nielsen, CB.; Johnsen, M.; Arnbjerg, J.; Pittelkow M.; McIlroy, SP.; Ogilby, PR.; Jrgensen, M. *J Org. Chem.* **2005**, *70*, :7065. Synthesis of fulleropyrrolidines and fulleropyrrolidiums, Bosi, S.; Feruglio, L.; Milic, D.; Prato, M. *Eur. J. Org. Chem.* **2003**, 4741.

acid (111 mg, 1.25 mmol) in chlorobenzene (100 mL) was refluxed under N<sub>2</sub> for 4 h. After evaporation of the solvent, the residue was subjected to chromatograph purification on a silica gel column. Elution with toluene gave little unchanged C<sub>60</sub>. Fraction containing mono adduct was collected with PhMe/EtOAc (1:2) eluent. One fraction of bisadducts consisting mixture of regioisomers was then collected with EtOAc eluent. Each sample was precipitated from toluene solution with methanol or hexane, and gave monofulleropyrrolidine (115 mg, 27%), bisfulleropyrrolidine (90 mg, 15%). **Quaternization of neutral fulleropyrrolidines** was achieved by heating a solution of mono or bis fulleropyrrolidine (0.05 mmol) in chloroform (2 mL) and MeI (1.5 mL) in a screw-topped Schlenk tube under N<sub>2</sub>. Reaction mixture was kept at 80 °C for 40 h. After evaporation of the solvent, the product was dissolve in chloroform and precipitated with hexane. After thoroughly washed with n-hexane, black fulleropyrrolidiums, ETL-1 or ETL-2, was obtained in quantitative yield.

**Monofulleropyrrolidine** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  2.78 (s, 3H, NC<u>H</u><sub>3</sub>), 3.34 (s, 3H, OC<u>H</u><sub>3</sub>), 3.36 (s, 3H, OC<u>H</u><sub>3</sub>), 3.40 (s, 3H, OC<u>H</u><sub>3</sub>), 3.48-3.50 (m, 2H, OC<u>H</u><sub>2</sub>), 3.53-3.58 (m, 4H, OC<u>H</u><sub>2</sub>), 3.63-3.80 (m, 10H, OC<u>H</u><sub>2</sub>), 3.86 (t, *J* = 5.5 Hz, 2H, OC<u>H</u><sub>2</sub>), 3.05-4.18 (m, 4H, OC<u>H</u><sub>2</sub>), 4.27-4.32 (m, 2H, OC<u>H</u><sub>2</sub>), 4.37-4.40 (m, 2H, OC<u>H</u><sub>2</sub>), 4.94 (d, *J* = 9.5 Hz, 1H, NC<u>H</u><sub>2</sub>), 5.56 (s, 1H, NC<u>H</u><sub>2</sub>), 6.77 (d, *J* = 8.5 Hz, 1H, Ar-<u>H</u>), 7.63 (d, *J* = 8.5 Hz, 1H, Ar-<u>H</u>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  39.89, 58.99, 59.00, 59.03, 59.05, 59.18, 59.19, 68.36, 69.25, 69.76, 69.83, 70.21, 70.35, 70.62, 70.72, 70.74, 71.95, 71.98, 72.05, 72.23, 73.18, 75.74, 77.20, 109.34, 123.31, 124.57, 134.82, 136.06, 136.49, 136.59, 139.47, 139.53, 140.12, 140.14, 141.19, 141.58, 141.67, 141.89, 141.99, 142.08, 142.11, 142.16, 142.28, 142.29, 142.54, 142.57, 142.63, 142.65, 143.00, 143.08, 144.36, 144.45, 144.61, 145.11, 145.12, 145.18, 145.23, 145.26, 145.31, 145.55, 145.76, 145.94, 146.07, 146.09, 146.12, 146.20, 146.27, 146.77, 146.95, 147.30, 152.20, 152.47, 154.15, 154.33, 155.16, 156.87. MALDI-TOF-MS (+): caled. for [C<sub>84</sub>H<sub>41</sub>NO<sub>9</sub>]<sup>7</sup>, 1208.225, found. [M]<sup>7</sup>, 1207.893

**Bisfulleropyrrolidine** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.55-2.88 (m, NC<u>H</u><sub>3</sub>), 3.29-3.40 (m, OC<u>H</u><sub>3</sub>), 3.42-4.00 (m, OC<u>H</u><sub>2</sub>&OC<u>H</u><sub>3</sub>), 4.06-4.68, 4.92-5.57, 5.74-5.75, 6.52-6.98, 7.35-7.49, 7.59-7.69, 7.73-7.88, 8.00-8.03; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 39.66-39.83 (m, N<u>C</u>H<sub>3</sub>), 53.21-53.43 (m), 58.97-59.22 (m), 68.17-68.43, 69.42, 69.70-69.94, 70.14-70.91, 71.90-72.35, 72.92-73.50, 75.34-76.00, 77.40-77.66, 109.12-109.48, 123.58-123.98, 124.42-124.61, 134.87, 136.53, 139.39, 140.76-141.93, 142.14, 142.00, 142.23, 142.30, 142.37, 142.51, 142.58, 142.95, 142.97, 143.38, 143.39, 143.58, 144.12, 144.36, 144.85, 144.96, 145.08, 145.21, 145.26, 145.44-145.74, 146.05, 146.07, 147.25, 147.47, 147.72, 147.84, 148.64, 148.77, 149.03, 150.75-151.39, 151.97-152.83, 153.66, 154.28-154.98, 155.54; MALDI-TOF-MS (+): calcd. for  $[C_{108}H_{82}N_2O_{18}]$ , 1695.809, found.  $[M-I]^+$ , 1695.929

**Fulleropyrrolidium** ETL-1 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 3.36 (s, 3H, OCH<sub>3</sub>), 3.38 (s, 3H, OCH<sub>3</sub>), 3.52-3.56 (m, 7H, OCH<sub>2</sub>&OCH<sub>3</sub>), 3.67-3.77 (m, 8H, OCH<sub>2</sub>), 3.80-3.84 (m, 2H, OCH<sub>2</sub>), 3.89 (m, 2H, OCH<sub>2</sub>), 3.97 (s, 3H, NCH<sub>3</sub>), 4.02 (d, J = 8.5 Hz, 2H, OCH<sub>2</sub>), 4.20-4.39 (m, 4H, OCH<sub>2</sub>), 4.48 (s, 3H, NCH<sub>3</sub>), 4.66-4.68 (m, 2H, OCH<sub>2</sub>), 5.80 (d, J = 12.5 Hz, 1H, NCH<sub>2</sub>), 6.84 (d, J = 13.0 Hz, 1H, NCH<sub>2</sub>), 6.88 (d, J = 9.0 Hz, 1H, Ar-<u>*H*</u>), 7.28 (d, J = 13.0 Hz, 1H, NC<u>*H*</u><sub>2</sub>), 7.71 (d, J = 8.5 Hz, 1H, Ar-<u>*H*</u>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 45.69, 53.44, 59.04, 59.07, 59.08, 59.28, 67.89, 68.44, 69.38, 69.96, 70.43, 70.54, 70.69, 70.72, 71.42, 71.65, 71.93, 71.97, 72.53, 72.56, 73.13, 73.64, 78.60, 108.66, 111.57, 127.48, 134.10, 134.75, 135.52, 136.11, 139.03, 139.87, 139.98, 140.26, 140.93, 141.24, 141.38, 141.43, 141.45, 141.62, 141.82, 142.03, 142.09, 142.11, 142.13, 142.35, 142.39,142.51, 142.52, 142.76, 142.84, 142.96, 143.01, 143.12, 143.33, 144.19, 144.23, 144.36, 144.42, 144.82, 144.89, 145.14, 145.26, 145.30, 145.45, 145.54, 145.61, 145.66, 145.77, 145.82, 145.96, 146.02, 146.13, 146.18, 146.35, 146.40, 147.42, 147.56, 149.32, 150.51, 151.18, 152.66, 153.66, 153.83, 155.77; MALDI-TOF-MS (+): calcd. for  $[C_{85}H_{44}NO_9]^+ \cdot \Gamma$ , 1350.16, found. [M-I]<sup>+</sup>, 1222.144; Anal. Calcd for C<sub>85</sub>H<sub>44</sub>INO<sub>9</sub>: C, 75.61; H, 3.28; N, 1.04. Found: C, 73.29; H, 2.76; N, 0.76.

**Fulleropyrrolidium** ETL-**2** (mixture of regioisomers) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>OD):  $\delta$  3.32-3.40 (m, OC<u>H</u><sub>3</sub>), 3.42-4.03 (m, OC<u>H</u><sub>2</sub>&OC<u>H</u><sub>3</sub>), 4.12-4.50 (m, OC<u>H</u><sub>2</sub>), 4.56-4.61 (m, OC<u>H</u><sub>2</sub>), 4.70-4.72 (m, OC<u>H</u><sub>2</sub>), 5.36-5.69 (m, NC<u>H</u><sub>2</sub>), 6.02-6.07, 6.68-6.97, 7.04-7.13, 7.20-7.21, 7.32-7.34, 7.37-7.61, 7.77-7.89, 7.98-8.04, 8.10-8.14, 8.27-8.31; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  45.28-46.47 (m), 53.21-53.43 (m), 58.99-59.49 (m), 66.06, 66.83, 68.45, 68.49-69.41, 69.51-70.89, 71.27-71.52, 71.96-72.06,

72.46-72.67, 73.55-73.84, 78.65, 78.75, 109.24, 109.35, 109.48, 111.29, 111.44, 136.24, 136.67, 140.04, 140.44, 140.84, 140.96, 141.13, 141.35, 141.58, 141.60, 141.67, 141.73, 141.77, 141.81, 141.83, 141.94, 142.14, 142.17, 142.21, 142.32, 142.38, 142.40, 142.51, 142.61, 145.38, 145.48, 145.59, 146.14, 146.20, 147.21, 147.40, 147.53, 147.79, 147.96-148.09, 148.40, 148.70-148.82, 149.08-149.32, 150.06, 151.57, 153.67-153.76, 155.68-155.89; MALDI-TOF-MS: calcd. for  $[C_{110}H_{88}N_2O_{18}]^{2+}\cdot 2\Gamma$ , 1979.69, found  $[M-2I-NMe_3]^+$  1666.278; Anal. Calcd for  $C_{110}H_{88}I_2N_2O_{18}$ : C, 66.74; H, 4.48; N, 1.42. Found: C, 66.07; H, 4.23; N, 1.35.

## 2. CV measurements

Cyclic voltammetry (CV) measurements were carried out in a one-compartment cell under  $N_2$ , equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and an Ag/Ag<sup>+</sup> reference electrode. Measurements were performed in THF solution containing Tetrabutylammonium Hexafluorophosphate (0.1 M) as a supporting electrolyte with a scan rate of 100 mV/s. All potentials were corrected against Fc/Fc<sup>+</sup>. Due to close vicinity of the electron-deficient cationic nitrogen to the fullerene core, the LUMO level of ETL-1 to that of ETL-2 has a small difference in 0.03 eV.



Figure S1. Cyclic voltammogram of ETL-1 (blue trace), ETL-2 (black trace), and  $PC_{61}BM$  (red trace) in THF.

## 3. UV-vis absorption



Figure S2. Absorption spectra of ETL-1 and ETL-2 in Methanol ( $5 \times 10^{-5}$  mol/L), the inset is the enlarged absorption spectra in the visible region from 400 to 700 nm.



Figure S3. MALDI-TOF mass spectra of ETL-1.



Figure S4. MALDI-TOF mass spectra of ETL-2.

# 4. Organic Field-Effect Transistors

Top contact OFETs were fabricated as typical top contact, bottom gate devices on silicon substrates. Heavily doped p-type silicon <100> substrates from Montco Silicon Technologies INC. with a 300 nm ( $\pm$ 5 nm) thermal oxide layer acted as a common gate with a dielectric layer. After cleaning the substrate by sequential ultrasonication in acetone, methanol, and isopropyl alcohol for 15 min fllowed by air plasma treatment, the different fullerene surfactant films were spin-coated from a 0.5 wt% chloroform solution in ambient. Interdigitated source and drain electrodes (W=1000 µm, L=12 µm) were defined by evaporating a 50 nm Au film through a shadow mask from the resistively heated Mo boat at 10<sup>-6</sup> Torr. OFET characterization was carried out in a N<sub>2</sub>–filled glovebox using an Agilent 4155B semiconductor parameter S6 analyzer. The field-effect mobility was calculated in the saturation regime from the linear fit of ( $I_{ds}$ )<sub>1/2</sub> vs V<sub>gs</sub>. The threshold voltage (V<sub>t</sub>) was estimated as the x intercept of the linear section of the plot of ( $I_{ds}$ )<sub>1/2</sub> vs V<sub>gs</sub> in the region of exponential current increase.



Figure S5. (a and b) Transfer characteristics ETL-1 and ETL-2. (c and d) Output current-voltage characteristics of ETL-1 and ETL-2.

#### 5. Work Function Measurements by XPS

Samples for work function analysis were prepared on glass substrates coated with ITO to ensure good electrical contact. Work functions were measured with a PHI Versa Probe X-ray photoelectron spectrometer (ULVAC-PHI, Kanagawa, Japan) employing a monochromatic focused Al-K<sub> $\alpha$ </sub> X-ray source and hemispherical analyzer. The Au 4f<sub>7/2</sub> (84.00 eV) and Cu 2p<sub>3/2</sub> (932.66 eV) photoemission peaks were used to calibrate the binding energy scale. A bias voltage (-5 V) was applied to the sample, and the location of the secondary electron cut-off was determined at normal emission by a linear extrapolation to the background level as described elsewhere.<sup>2</sup> To account for the instrument width, 0.14 eV were added to the work function values thus obtained. This procedure gives a work function for argon ion sputtered gold foil of 5.17 eV.



Figure S6. XPS spectra of Alumina with and without interfacial layers, and insert is the enlarged spectra.

<b>`</b>	Al	ETL-1/Al	ETL-2/A1
Secondary electron	1477.54	1478.16	1478.32
emission (eV)			
Work-Function (eV)	4.20	3.66	3.42

<sup>&</sup>lt;sup>2</sup> Schlaf, R.; Murata, H.; Kafafi, Z. H. J. Elect. Spec. Rel. Phen. 2001, 120, 149.