

Supporting information

***In-situ* Doping and Crosslinking of Fullerenes to Form Efficient and Robust Electron-Transporting Layer for Polymer Solar Cells**

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General. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk technique. All ¹H (500 MHz) and ¹³C (125 MHz) NMR spectra were recorded on a 15 Bruker AV500 spectrometer. Spectra were reported in parts per million from internal tetramethylsilane (δ 0.00 ppm) or residual protons of the deuterated solvent for ¹H NMR and from solvent carbon (e.g. δ 77.00 ppm for chloroform) for ¹³C NMR. AFM images under tapping mode were taken on a Veeco multimode AFM with a Nanoscope III controller. Cyclic voltammetry (CV) measurements were carried out in a one-compartment cell under N₂, equipped with a glassy-carbon working electrode, a 20 platinum wire counter electrode, and an Ag/Ag⁺ reference electrode. Measurements were performed in ODCB/MeCN (5:1 v/v) (0.5 mM) 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⁺. C₆₀ and PCBM were purchased from American Dye Source. The Matrix for MALDI-TOF-MS used 2:1 mixture of alpha-cyano-4-hydroxycinnamic acid (CHCA)/2,5-dihydroxybenzoic acid (DHB) in 25 acetonitrile. C₆₀ was purchased from American Dye Source. 4-vinylbenzyl Chloride was purchased from Sigma-Aldrich. Unless otherwise noted, materials were purchased from Aldrich Inc., and used after appropriate purification.

30 **Synthesis of 1,4-di(vinylbenzyl) fullerene (Full-s):** To a freeze-thaw degassed mixture of C₆₀ (2000 mg, 2.78 mmol) and 1-methylnaphthalene (11.8 mL, 83 mmol, 30 equiv.) in 250 mL THF, metal Potassium (271 mg, 6.95 mmol) was added in one portion. A dark red solution was produced after

stirring under argon at room temperature for 5 h. 4-Vinylbenzyl chloride (8.5 ml, in 90% purity, ~ 54 mmol) was then added dropwisely. After stirring for another 3.5 h, the reaction mixture was heated at 50 °C overnight then quenched with degassed, saturated aqueous NH₄Cl (2 mL). The resulting concentrated mixture was precipitated into methanol. The crude product was pre-absorbed in silica gel then separated with a silica gel column (eluent: first with CS₂/hexane = 1/5, then CS₂/hexane = 1/2, then CS₂) to afford a compound in 45 % yield. **Full-s** ¹H 500 MHz NMR (CDCl₃): δ 3.88 (s, 4H, CH₂), 5.27 (dd, *J*₁ = 5.0 Hz and *J*₂ = 0.9 Hz, 2H), 5.27 (dd, *J*₁ = 8.25 Hz and *J*₂ = 0.9 Hz, 2H), 6.76 (dd, *J*₁ = 3.30 Hz and *J*₂ = 10.8 Hz, 2H), 7.56 (m, 8H, Ar-H) ¹³C NMR (125 MHz, CDCl₃): δ 48.44, 60.47, 114.01, 128.26, 131.22, 135.76, 138.84, 140.54, 141.98, 142.45, 142.64, 142.97, 143.09, 143.19, 143.71, 143.94, 144.12, 144.25, 144.27, 144.37, 144.67, 144.69, 144.77, 145.01, 145.50, 146.14, 146.92, 146.97, 147.17, 148.63, 148.64, 151.72, 157.71; MALDI-TOF-MS (+): calcd. for [C₇₆H₁₈O₂]⁺, 954.98, found. [M-H]⁻, 953.20, [M-vinylbenzyl]⁻, 836.36

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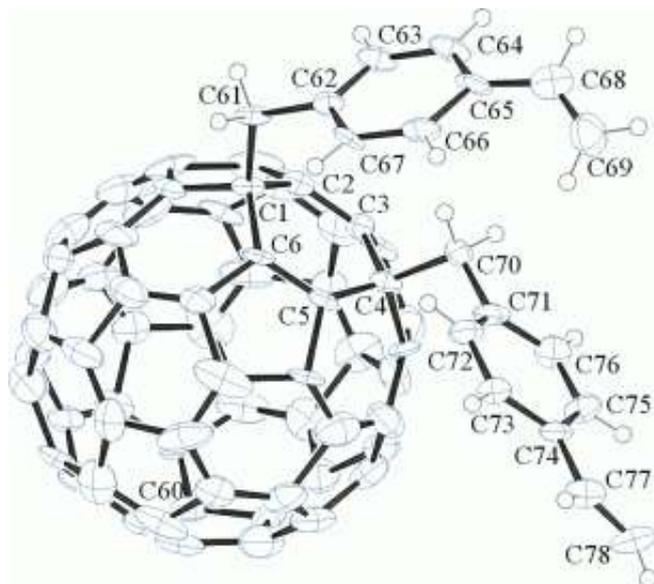


Figure S1. ORTEP of the structure with thermal ellipsoids at the 50% probability level. Black red plate crystals of **full-s** suitable for single-crystal X-ray diffraction were obtained by slow evaporation of hexane/carbon disulfide solution.

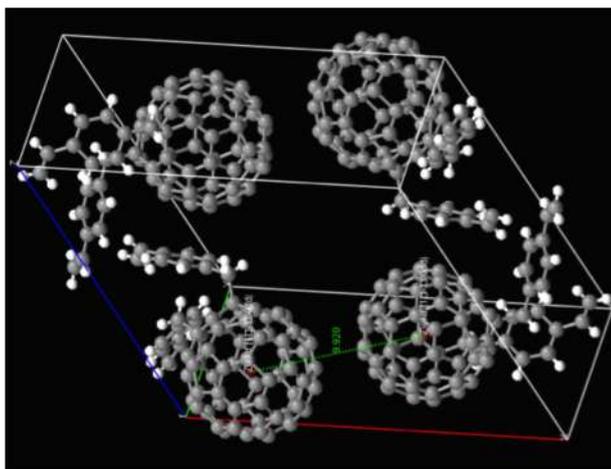


Figure S2. Single-crystal analysis of **full-s** showed the closest centre-to-centre distance of 0.99 nm for two fullerenes.

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Table S1: Crystallographic data for the structures provided.

Empirical formula	C78 H18	
Formula weight	954.92	
Temperature	100(2) K	
10 Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 2 ₁ /c 1	
Unit cell dimensions	a = 21.462(11) Å	α = 90°.
	b = 10.226(5) Å	β = 109.458(13)°.
	c = 19.538(10) Å	γ = 90°.
15 Volume	4043(4) Å ³	
Z	4	
Density (calculated)	1.569 Mg/m ³	
Absorption coefficient	0.090 mm ⁻¹	
20 F(000)	1944	
Crystal size	0.30 x 0.17 x 0.05 mm ³	
Theta range for data collection	1.73 to 25.19°.	
Index ranges	-25<=h<=25, -11<=k<=12, -23<=l<=23	
Reflections collected	21316	
25 Independent reflections	6814 [R(int) = 0.1598]	
Completeness to theta = 25.00°	93.5 %	
Max. and min. transmission	0.9955 and 0.9735	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6814 / 60 / 705	
30 Goodness-of-fit on F ²	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.1487, wR2 = 0.3398	

R indices (all data) $R1 = 0.2784$, $wR2 = 0.4411$
Extinction coefficient 0.010(2)
Largest diff. peak and hole 0.832 and $-0.466 \text{ e.}\text{\AA}^{-3}$

Fabrication and characterization of OTFT devices: A top contact OTFT devices were fabricated on silicon substrates. Heavily p-doped Si/SiO₂ (300nm) substrates were purchased from Montco Silicon Technologies Inc. The substrates were cleaned by sequential ultra-sonication in acetone, methanol, and isopropyl alcohol. A thermally crosslinked divinyltetramethylsiloxane-bis(benzocyclobutene) (BCB) (Dow Chemicals, Product# XU-13005.02) layer was used to passivate the surface hydroxyl groups on the SiO₂ gate dielectric. The BCB diluted in toluene was spin-coated at 4000 rpm for 60 s. The film was annealed at 250 °C for 4 h under nitrogen for crosslinking. The thickness of the BCB film was 12 nm. The Full-x (bis-FPI) films were prepared from a 2 wt % chlorobenzene solution by spin-coating (5000 rpm for 120s). The gold (50 nm thick) electrodes were deposited on top of the fullerene films by thermal evaporation at 1.0 Å/s through a shadow mask under high vacuum (5.0×10^{-7} torr). The devices were characterized in a glove box with an Agilent 4155B semiconductor parameter analyzer. Charge carrier mobility was calculated with a linear fit of the saturation region of the square root of I_{ds} versus V_{gs} using the standard equation: $I_{ds} = [(\mu WC_0/2L)/(V_g - V_t)^2]$, where W , C_0 , and L are channel width (1000 μm), capacitance of gate dielectrics (10.4 nF/cm²) and channel length (20 μm), respectively. Figure S4a and S4b showed the linear fit of the saturation region of the square root of I_{ds} versus V_{gs} .

The conductivity was derived from two-terminal measurements with the equation of $\sigma = (L/A)(I_d / V_d)$, where L and A are the channel length and cross-sectional area of the devices, respectively. The conductivities calculated from the slope of V_d - I_d curves (Figure S4e and S4f) at zero gate voltage are summarized in Table 2 and Table S3. The slope was estimated with a linear fit of V_d - I_d curves.

Fabrication of PSCs: ITO coated glass substrates were cleaned by sequential ultrasonication in acetone, methanol, and isopropyl alcohol, and then treated with oxygen plasma. The ETLs (Full-x and Full-x (bis-FPI)) were prepared from a 2 wt % chlorobenzene solution by spin-coating (2000 rpm and 5000 rpm for 120s). The substrates were submitted to a thermal annealing (210 °C for 30 min) under N₂ atmosphere. The active layers were deposited on ETLs by spin coating the PIDT-PhanQ:PC71BM

(1:3, weight ratio) solution (40 mg/ml in DCB) and then annealed at 110 °C for 10 min in the glove box. A MoO₃ (5 nm) was then deposited via thermal evaporation at a rate of 0.2 Å/s. Afterward, a metal electrode (Ag) (100 nm) was vacuum-deposited at a rate of 2 Å/s.

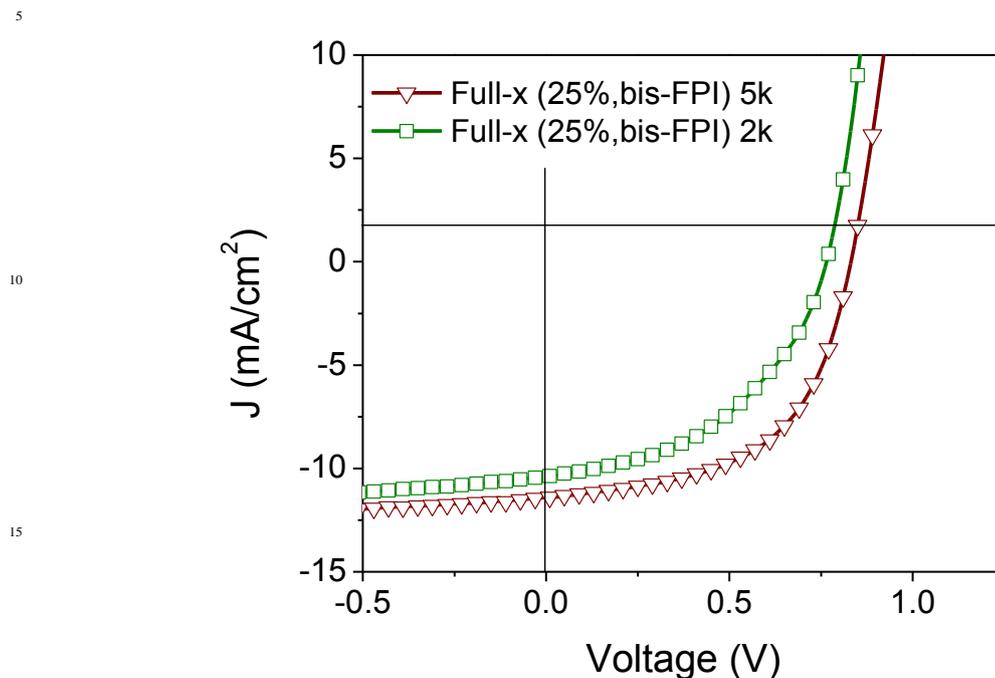


Figure S3. The thickness dependence of device performance for Full-x (25%, bis-FPI) fabricated by two different spin speed (5k rpm for 12 nm and 2k rpm for 24 nm).

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Table S2. Summary of device performance with different thickness of ETLs.

ETL	PCE (%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF
Full-x (25%, bis-FPI), 12 nm	5.26	0.83	11.4	0.56
Full-x (25%, bis-FPI), 24 nm	3.66	0.76	10.4	0.46

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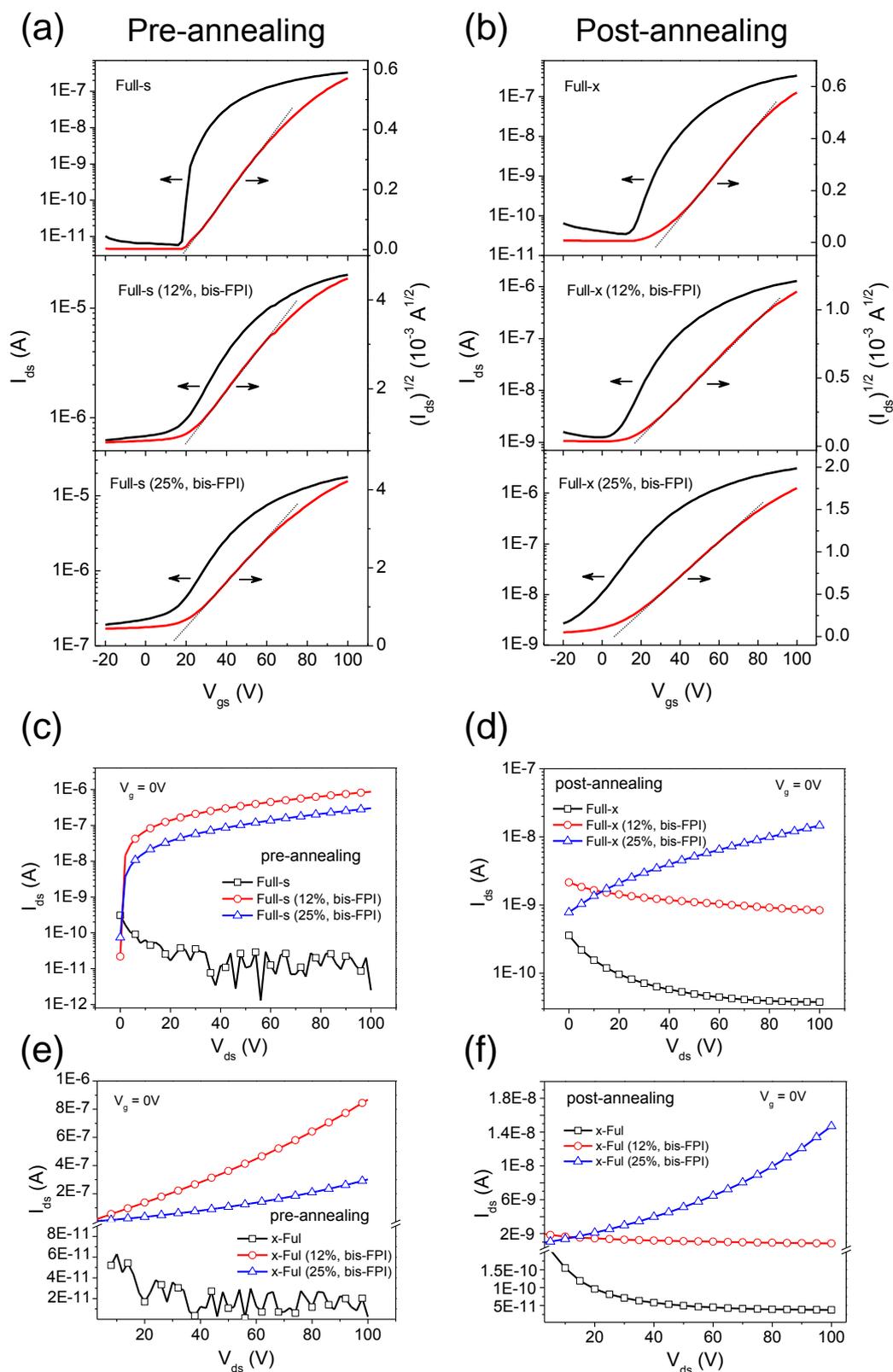


Figure S4. (a) Transfer characteristics of OTFT devices at varying bis-FPI concentration for Full-s (pre-annealing: before crosslinking) and (b) for Full-x (post-annealing: after crosslinking). (c, d) output characteristics for the same devices before and after crosslinking in semi-log scale of I_{ds} and (e, f) linear scale of I_{ds} .

Table S3. Summary of the performance of pre-annealed OFET devices based on various ETMs.

ETL	σ (S/m)	μ (cm ² /V·s)	$I_{\text{on}}/I_{\text{off}}$	V_t (V)
Full-s	1.3×10^{-7}	3.4×10^{-4}	5.6×10^4	21
Full-s (12%, bis-FPI)	9.1×10^{-3}	1.5×10^{-2}	3.2×10^1	9
Full-s (25%, bis-FPI)	2.0×10^{-3}	8.1×10^{-3}	9.3×10^1	13

Measurements of the capacitance density of gate dielectrics: The total capacitance densities of the gate dielectric layers were measured from parallel-plate capacitors with p⁺⁺Si/SiO₂/BCB/Ag and p⁺⁺Si/SiO₂/Ag structures using the equation: $1/C_0 = [(d_{\text{SiO}_2}/k_{\text{SiO}_2}) + (d_{\text{BCB}}/k_{\text{BCB}})](1/\epsilon_0)$, where ϵ_0 : vacuum permittivity, k : the dielectric constant of the gate dielectric materials, d : thickness). Capacitance-voltage measurements were performed using a HP 4284A LCR meter at room temperature for frequencies from 500 Hz to 300 KHz. The capacitance density vs. frequency for SiO₂ (300 nm) and SiO₂ (300 nm)/BCB (12 m) is shown in **Figure S4**. The capacitance densities of SiO₂ and SiO₂/BCB were ~10.9 and 10.4 nF/cm², respectively. The dielectric constant of the BCB was extracted from the accumulation capacitance of the capacitance-voltage curves by assuming that the total capacitance corresponds to the series combination of BCB and SiO₂ ($1/C_{\text{total}} = 1/C_{\text{SiO}_2} + 1/C_{\text{BCB}}$), where $C = \epsilon_0 k A/d$. The active area of device (A) is 3.14×10^{-2} cm². The dielectric constant of BCB we calculate is ~2.7.

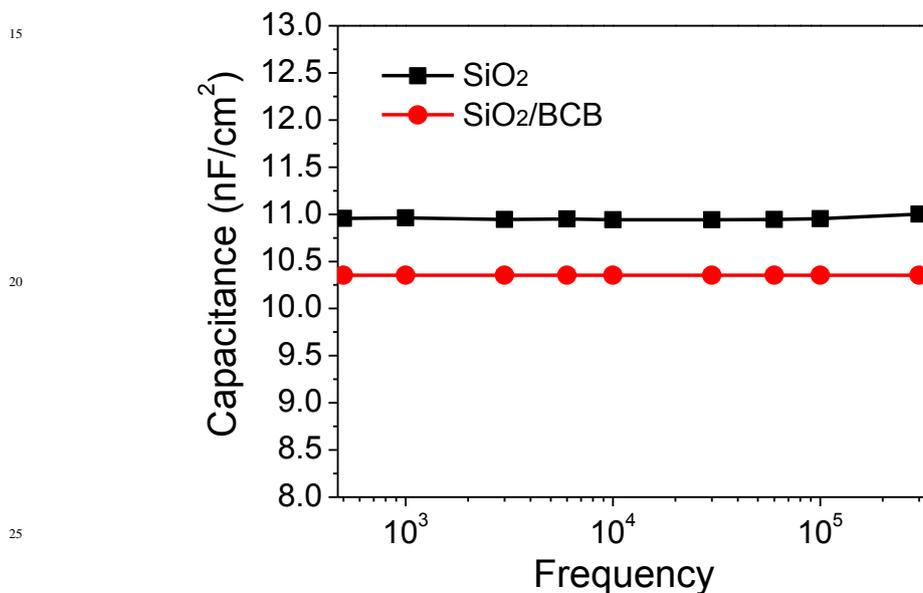


Figure S5. Capacitance density vs. frequency for SiO₂ and SiO₂/BCB gate dielectrics.