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Electronic Supporting Information (ESI)

Neutral amine based alcohol-soluble interface materials for inverted polymer solar cells: realizing high performance and overcoming solvent erosion

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1. Chemicals and Materials

All reagents, unless otherwise specified, were purchased from commercial sources and used without further purification. Tetrahydrofuran (THF) and toluene were purified by distillation from Na-K under dry argon. PTB7 was obtained from 1-material chemscitech, $PC_{71}BM$ was purchased from American Dye Source Incorporated.

2. Measurement and Characterization

^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz AVANCE III with tetramethylsilane as an internal reference, in deuterated chloroform or deuterated methanol respectively. Mass spectra were obtained on a Finnigan LCQ mass spectrometer. UV-vis absorption spectra were recorded on a mapada UV-3300 spectrophotometer. Cyclic voltammetry (CV) was carried out on a CHI600D electrochemical workstation with a platinum working electrode of 2 mm diameter and a platinum wire counter electrode at a scan rate of 50 mV s^{-1} against a solution of 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in anhydrous acetonitrile. The film for electrochemical measurements was coated from its methanol solution. The tapping-mode AFM images were obtained by using a scanning probe microscope (Dimension3100V).

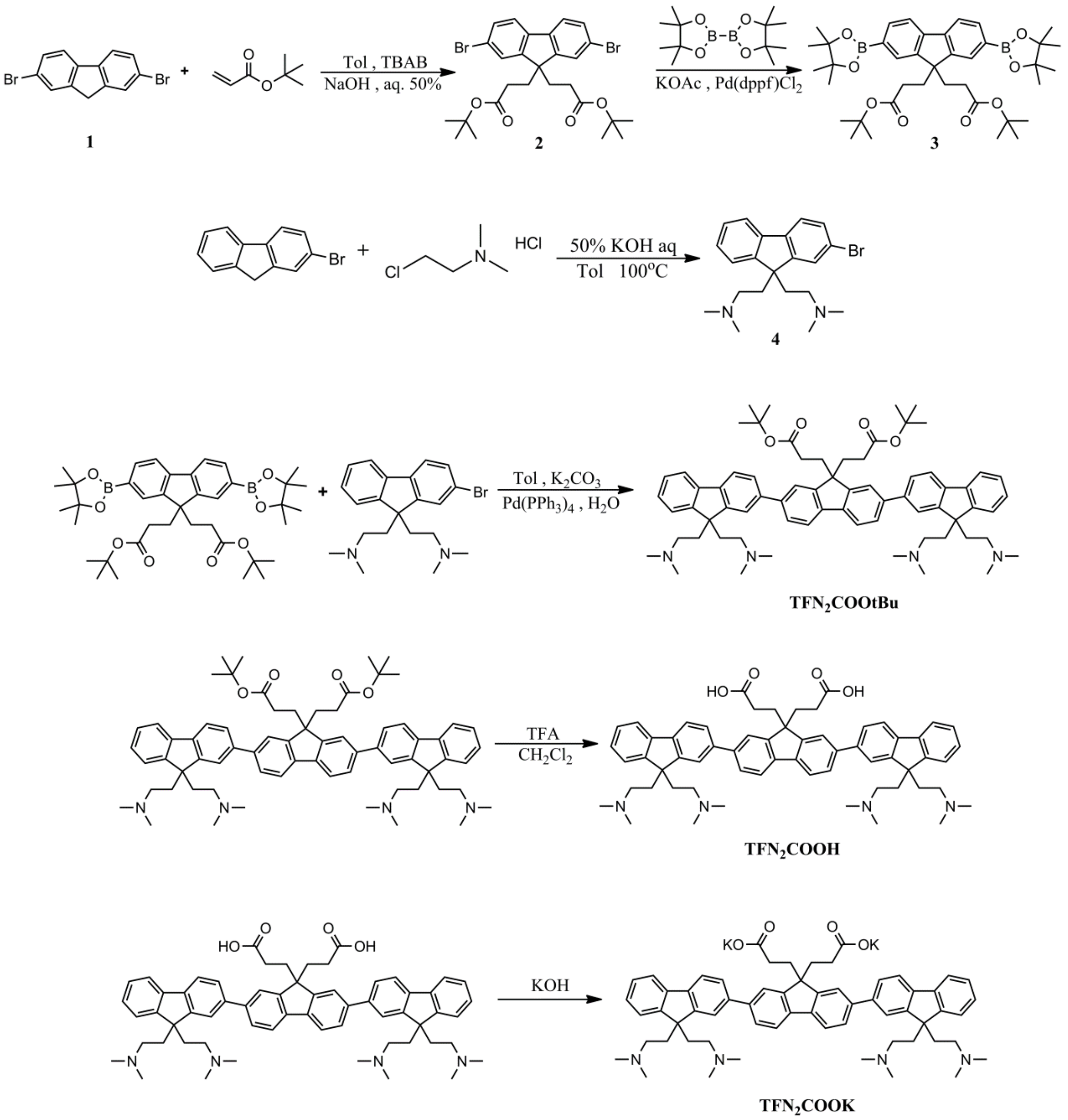
3. Device fabrication

The inverted device structure was ITO substrate/interlayer/PTB7:$PC_{71}BM$/MoO_3/Al. ITO substrates were cleaned by sonication in detergent, deionized water, acetone and isopropyl alcohol and dried in a nitrogen stream. The cleaned ITO substrates were then treated with UV/ozone for 20 min. Then the cathode interlayers were spin-coated on the treated ITO substrate at 4000 rpm from their solutions in methanol. The optimized concentrations for spin casting $TFN_2COOtBu$, TFN_2COOH, and TFN_2COOK solutions were found to be at 6.0 mg mL^{-1}, 2.5 mg mL^{-1}, 0.5 mg mL^{-1}. The PTB7 were blended with $PC_{71}BM$ and dissolved in chlorobenzene (CB) with an addition of small amount of 1,8-diiodoctane (DIO) (CB:DIO = 97:3, v/v). The blended ratio of PTB7:$PC_{71}BM$ was 1:1.5 by weight. The solutions were spin-coated onto the ITO interlayer at 1500 rpm. The thickness of the active layers was about 100 nm. Subsequently, the film was transferred into a thermal evaporator. Then, 10 nm of MoO_3 layer and 100 nm of Al layer were deposited through a shadow mask (defined the active area of the devices 0.06 cm^2) onto the photoactive layer by thermo-evaporation in a vacuum chamber with base pressure 2×10^{-6} mbar. All device fabrication processes are carried out in a N_2-filled glove box.

The conventional device structure was ITO substrate/PEDOT:PSS/PTB7:$PC_{71}BM$/ Interlayer/Al, and device fabrication process was almost the same with the I-PSCs. Only PEDOT:PSS was spin-coated on the treated ITO substrates at 4000 rpm from their solution in water. The optimized concentrations for spin casting $TFN_2COOtBu$, TFN_2COOH, and TFN_2COOK solutions were found to be at 0.5 mg mL^{-1}, 1.0 mg mL^{-1}, 0.5 mg mL^{-1}.

The *J-V* characteristics were recorded with a Keithley 236 source meter. The spectral response was measured with a commercial 40 photomodulation spectroscopy setup (Oriel). A calibrated Si photodiode was used to determine the photosensitivity. PCE was measured under an AM 1.5G solar simulator. The power of the sun simulation was calibrated before the measurement using a standard silicon solar cell.

4. Synthesis and characterization



Scheme S1 Synthetic routes of TFN$_2$COOtBu, TFN$_2$COOH and TFN$_2$COOK

9,9-bis(3’-(tert-butylpropionate))-2,7-dibromofluorene(2)

To a three-neck round-bottom flask, 2,7-dibromofluorene (5.00 g, 15.5mmol), tetrabutylammonium bromide (125 mg, 0.445 mmol), and toluene (30 mL) were added under nitrogen atmosphere. After 60 min, 12 mL of 50 wt % NaOH aqueous solution was added dropwise, and the solution was stirred for 60 min. After that, tert-butyl acrylate (7.9 g, 61.6 mmol) was added dropwise, and the mixture was stirred at 25 °C overnight. After this time, the reaction product was extracted with dichloromethane, washed three times with water, and dried with anhydrous Na$_2$SO$_4$. After solvent removal the product was purified by column chromatographic to give 6.25 g of white solid with a 70% yield. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.50-7.52 (d, *J*=8.0 Hz, 2H), 7.50-7.47 (m, 4H), 2.32-2.28 (t, *J*=8.0 Hz, 4H), 1.48-1.44 (t, *J*=8.0 Hz, 4H), 1.33 (s, 18H).

9,9-bis(3'-(tert-butylpropionate))-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fluorene(3)

Compound 2 (3.67 g, 6.3 mmol), potassium acetate (4.4 g, 44 mmol), bis(pinacolato) – diboron (4.0 g, 15.8 mmol), [1,1-bis(diphenylphosphino)ferrocene]-dichloropalladium(II) (315 mg, 0.5 mmol) and dioxane (60 mL) were placed in a 150 mL two-neck flask under nitrogen atmosphere. The reaction mixture was stirred at 85 °C overnight. After this time, the product was extracted three times with dichloromethane, the organic layers were combined and washed with water and then dried with anhydrous sodium sulfate. The organic solvent was removed by vacuum evaporation and the crude was purified by column chromatography on silica with dichloromethane as eluent, yielding compound 3 (3.16 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.83-7.81 (d, *J*=8.0 Hz, 2H), 7.78 (s, 2H), 7.72-7.71 (d, *J*=4.0 Hz, 2H), 2.40-2.36 (t, *J*=8.0 Hz, 4H), 1.43-1.39 (t, *J*=8.0 Hz, 4H), 1.39 (s, 24H), 1.30(s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 172.9, 147.9, 143.8, 134.4, 129.0, 129.0, 119.7, 83.9, 79.9, 53.5, 34.5, 30.0, 28.0, 28.0, 24.9.

9,9-bis(2'-(N,N-dimethylamino)ethyl)-2-bromofluorene (4)

2-bromofluorene (7.35 g, 30 mmol) and 2-chloro-N,N-dimethyl-ethyl amine hydrochloride (17.28 g, 120 mmol) were placed in a 500 mL two-neck flask under nitrogen atmosphere. Then, a KOH aqueous solution (120 mL, 50%, wt) and toluene (100 mL) were injected. The reaction mixture was stirred at 100 °C overnight. After cooling to room temperature, water was poured into the mixture to dissolve the salt and extracted with dichloromethane. The organic extraction was washed with brine and dried over anhydrous sodium sulfate, and the organic solvent was removed by vacuum evaporation. The residue was purified by column chromatography on silica with dichloromethane/methanol/ triethylamine (10:1:0.1, v) as eluent, yielding compound 4 (7.50 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.69 (m, 1H), 7.59(d, *J*=8.0 Hz, 1H), 7.54 (s, 1H), 7.51 (m, 1H), 7.39-7.36 (m, 3H), 2.24 (m, 4H), 2.05 (s, 12H), 1.56 (m, 4H).

TFN$_2$COOtBu

To a mixture of compound 4 (3.6 g, 7.2 mmol), compound 3 (1.68 g, 3.0 mmol) and Pd(PPh$_3$)$_4$ (90 mg, 0.08 mmol) was added degassed toluene (45 mL) and 2 M potassium carbonate aqueous solution (15 mL). The mixture was refluxed at 90 ^{o}C for 24 h under nitrogen. After cooling to room temperature, the mixture was extracted three times with dichloromethane. Then, the organic layers was washed with water and dried with anhydrous Na$_2$SO$_4$. The organic solvent was removed by vacuum evaporation and the residue was purified by column chromatographic on silica with dichloromethane/methanol/triethylamine (5:1:0.1), yielding compound TFN$_2$COOtBu (930 mg, 30%) as a light yellow solid. ^{1}H NMR (400 MHz, CD$_3$OD, δ): 7.93-7.91 (d, *J*=8.0 Hz, 2H), 7.88-7.86 (d, *J*=8.0 Hz, 4H), 7.82-7.76 (m, 8H), 7.53-7.52 (d, *J*=4.0 Hz, 2H), 7.42-7.36 (m, 4H), 2.56-2.52 (t, *J*=4.0 Hz, 4H), 2.49-2.35 (m, 8H), 2.04 (s, 24H), 1.65-1.53 (m, 12H), 1.24 (s, 18H). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 172.9, 149.5, 149.2, 149.0, 140.7, 140.6, 140.5, 140.2, 140.2, 127.7, 127.5, 126.9, 126.8, 122.9, 121.5, 121.2, 120.4, 120.2, 120.0, 80.1, 77.2, 54.0, 53.9, 52.4, 45.1, 38.0, 34.8, 30.2, 28.0. HRMS (ESI) *m/z*: [M+H]$^+$ calcd for C$_{69}$H$_{87}$N$_4$O$_4$, 1035.6727; found, 1035.6710.

TFN$_2$COOH

In a 250 ml flask, TFN$_2$COOtBu (0.3 g, 0.3 mmol) was dissolved in CH$_2$Cl$_2$ (150 mL). After addition of trifluoacetic acid (12 mL), the mixture was stirred overnight at room temperature. After removal of the solvent, the residue was dissolved in deionized water. Then, KOH aqueous solution was added to adjust the pH of the reaction mixture to about 8.0, and plenty of white flocculent precipitate formed in one hour. After centrifuging the mixture and removing supernatant liquor, the resulting product was washed with deionized water three times and dried in vacuum at 100 ^{o}C for 48 h, giving 0.205 g of light yellow solid with a 74% yield. ^{1}H NMR (400 MHz, CD$_3$OD, δ): 8.10-8.02 (d, *J*= 32.0 Hz, 4H), 7.91-7.88 (t, *J*=7.2 Hz, 4H), 7.84-7.81 (t, *J*=6.8 Hz, 4H), 7.76-7.74 (d, *J*=8.0 Hz, 2H), 7.57-7.55 (d, *J*=8.0 Hz, 2H), 7.45-7.38 (m, 4H), 3.00-2.97 (t, *J*=7.6 Hz, 4H), 2.71-2.64 (m, 4H), 2.45-2.50 (m, 4H), 2.28 (s, 24H), 2.07 (m, 4H), 1.80 (m, 4H), 1.65-1.61 (t, *J*=8.0 Hz, 4H). ^{13}C NMR (100 MHz, DMF, δ): 176.5, 151.3, 150.0, 149.8, 140.9, 140.8, 140.7, 140.5, 140.3, 127.8, 127.7, 127.0, 126.7, 123.3, 122.2, 121.5, 120.7, 54.9, 53.9, 52.7, 49.1, 44.0, 36.7, 36.4. HRMS (ESI) *m/z*: [M+H]$^+$

calcd for $C_{61}H_{71}N_4O_4$, 923.5475; found, 923.5528.

TFN_2COOK

TFN_2COOH (100 mg, 0.108 mmol) was placed in a 50 mL flask with 20 mL deionized water in it. Then, 2 mL aqueous solution of KOH (12.1 mg, 0.216 mmol) was added. After the reactant was dissolved completely, the water was removed by vacuum evaporation. The resulting product was dried in vacuum at 100 °C for 48 h to yield TFN_2COOK (80 mg, 74%). ^1H NMR (400 MHz, CD_3OD, δ): 7.91 (s, 2H), 7.88-7.87 (d, *J*=7.2 Hz, 6H), 7.83-7.81 (d, *J*=7.6 Hz, 4H), 7.74-7.72 (d, *J*=8.4 Hz, 2H), 7.54-7.53 (d, *J*=7.2 Hz, 2H), 7.43-7.36 (m, 4H), 2.62-2.50 (m, 8H), 2.43-2.36 (m, 4H), 2.14 (s, 24H), 1.78-1.65 (m, 8H), 1.59-1.55 (m, 4H). ^{13}C NMR (100 MHz, CD_3OD, δ): 181.2, 150.4, 148.9, 148.5, 141.2, 140.8, 140.4, 140.3, 140.0, 127.4, 127.3, 126.7, 126.1, 122.6, 121.5, 121.0, 120.0, 119.8, 119.7, 54.6, 53.7, 52.1, 43.7, 36.9, 36.7, 32.7. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{61}H_{71}N_4O_4$, 923.5475; found, 923.5528.

5. Figures and Tables

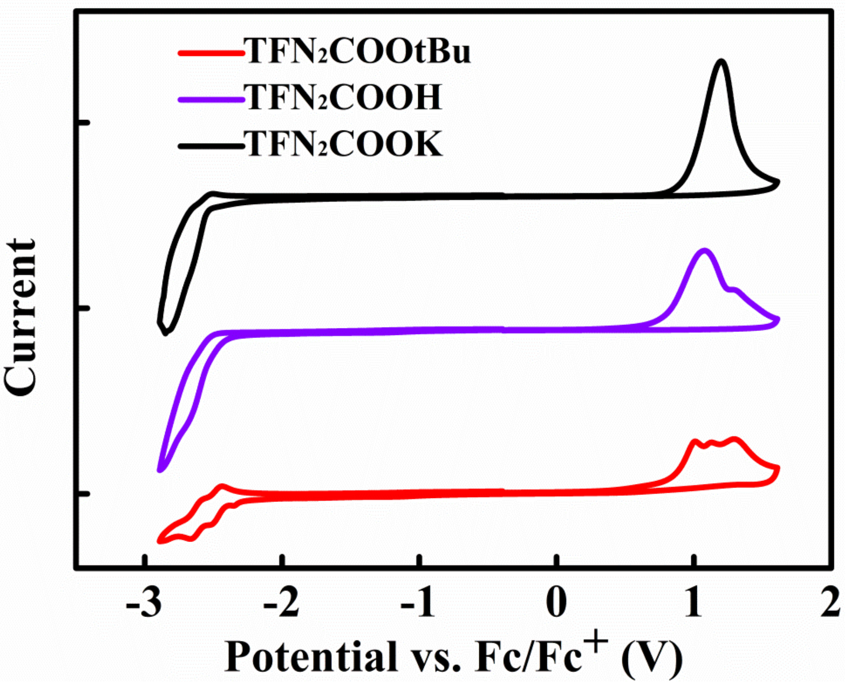


Fig. S1 Cyclic voltammogram of $TFN_2COOtBu$, TFN_2COOH, and TFN_2COOK in an acetonitrile solution of 0.1 M Bu_4NPF_6 at a scan rate of 50 mV s^{-1}

Table S1 UV-vis absorption, and electrochemical properties of the interlayer materials.

compound	$\lambda_{abs}{}^{a}$ [nm]	$\lambda_{abs}{}^{b}$ [nm]	$E_g{}^{opt}$ [eV]	$E_g{}^{CV}$ [eV]	HOMO[c] [eV]	LUMO[d] [eV]
$TFN_2COOtBu$	350	352	3.19	3.15	-5.62	-2.47
TFN_2COOH	350	366,382	3.18	3.15	-5.52	-2.37
TFN_2COOK	350	362	3.18	3.34	-5.64	-2.30

[a] In methanol solution, [b] In solid-state films, $E_g{}^{opt}$ is estimated from onset wavelength of optical absorption in methanol solution, [c] $E_{HOMO} = -(E_{ox} - E_{Fc/Fc^+} + 4.80)$ eV, [d] $E_{LUMO} = -(E_{red} - E_{Fc/Fc^+} + 4.80)$ eV.

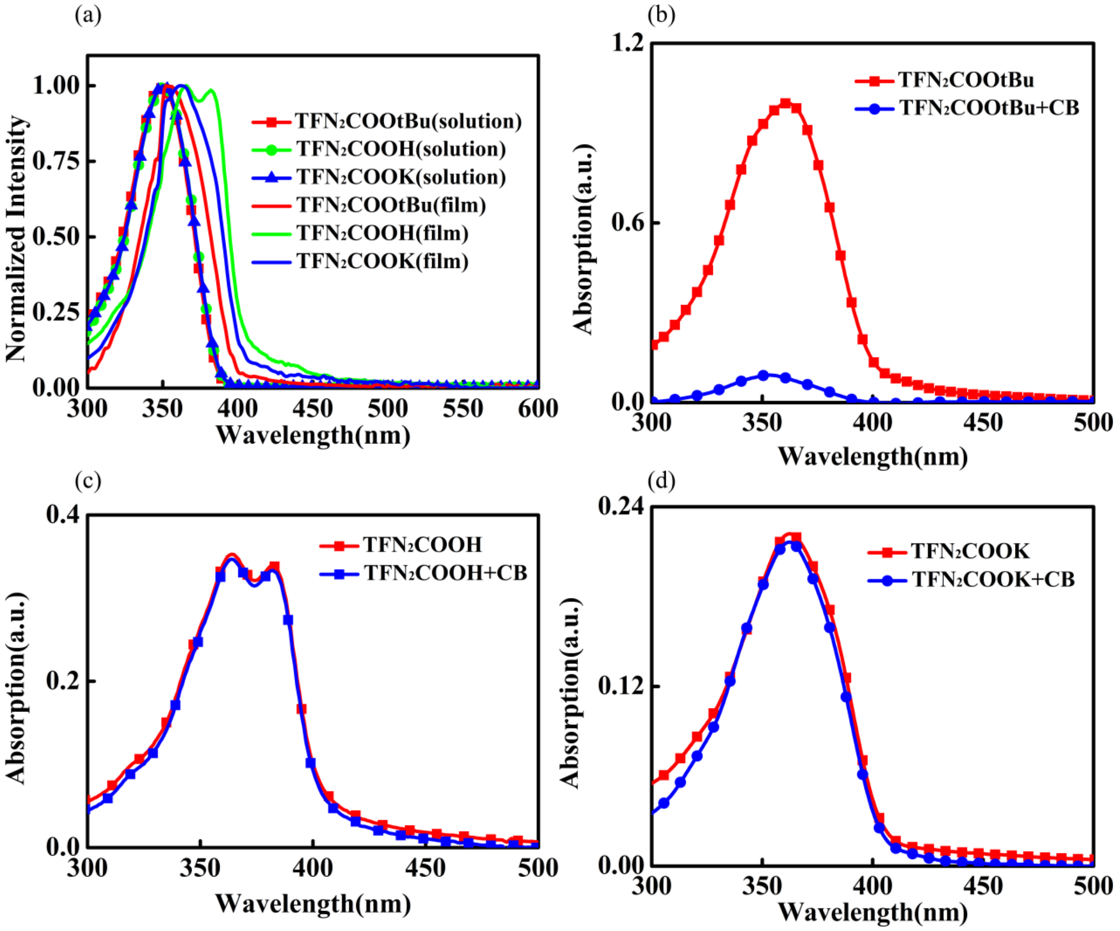


Fig. S2 (a) Normalized UV-vis absorption spectra of $TFN_2COOtBu$, TFN_2COOH, and TFN_2COOK solution and film; (b), (c), (d) UV-vis absorption spectra of $TFN_2COOtBu$, TFN_2COOH, and TFN_2COOK films before and after washing by chlorobenzene, respectively.

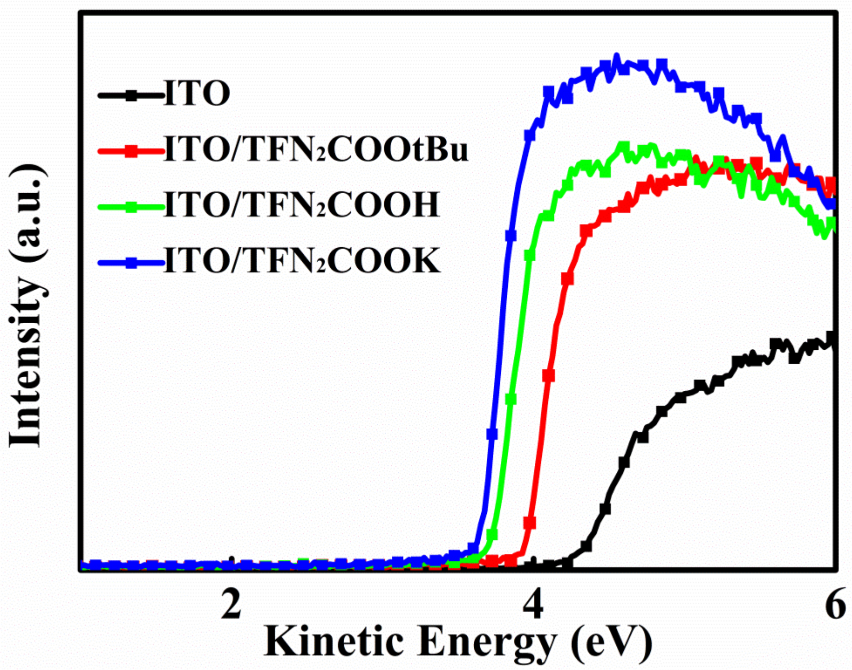


Fig. S3 UPS spectra of bare ITO, ITO/ $TFN_2COOtBu$, ITO/ TFN_2COOH, and ITO/ TFN_2COOK thin films.