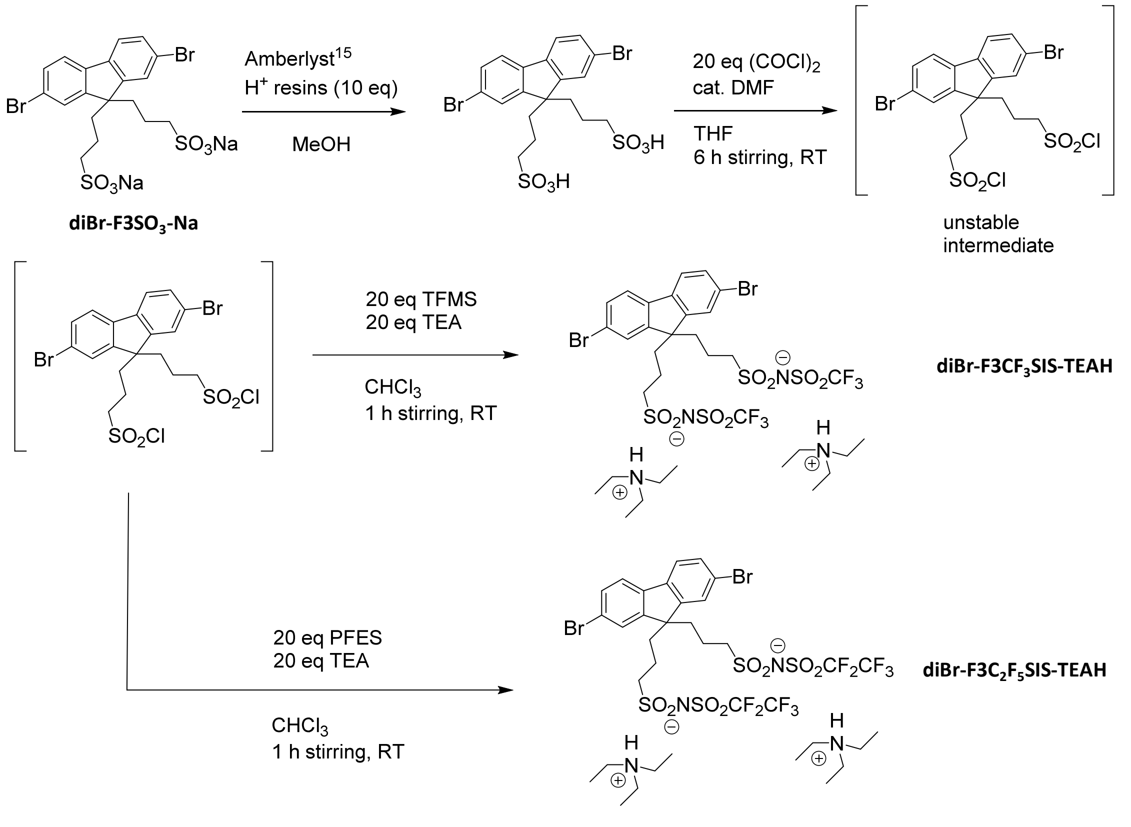
Electronic Supplementary Material (ESI) for Materials Horizons.

Supplementary Information S1

Materials. All reaction starting materials and reagents are either purchased from Sigma-Aldrich Pte Ltd or Tokyo Chemical Industry Ltd unless otherwise stated. diBr-F3SO_3-Na and diEs-mTFF starting monomers are synthesized according to reported procedures in Tang et al.[1] diEs-TFB starting monomer is obtained from Cambridge Display Technology Ltd/ Sumitomo Chemical Co.

Synthesis of 9,9-bis(3'-sulfonyl(trifluoromethanesulfonyl)imidopropyl)-2,7-dibromofluorene triethylammonium salt (diBr-F3CF_3SIS-TEAH) and 9,9-bis(3'-sulfonyl(pentafluoroethanesulfonyl)imidopropyl)-2,7-dibromofluorene triethylammonium salt (diBr-F3C_2F_5SIS-TEAH)

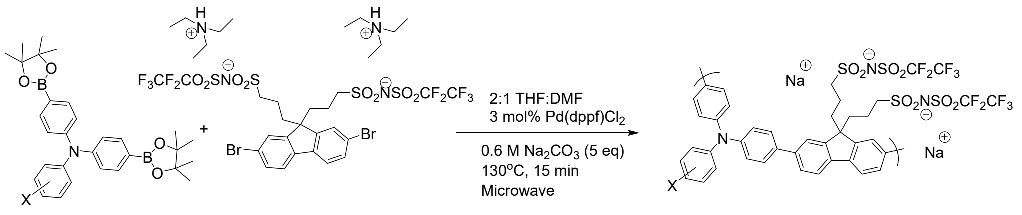


To a 100-mL Nalgene bottle, 3.5 g (5.7 mmol) of 9,9-bis(3'-sulfonatopropyl)-2,7-dibromofluorene sodium, diBr-F3SO_3-Na was dissolved in 70 mL of methanol (MeOH). 20 molar equivalents of Amberlyst 15 hydrogen form H^+ resins (24.3 g, 114.3 mmol) were washed to pH 7 with deionized water and added to the monomer solution. The solution was left on a mechanical roller for 6 h at RT. Upon completion, the solution was filtered through a 0.2-µm nylon syringe filter into a round-bottomed flask (rbf). The solution was concentrated yielding 9,9-bis(3'-sulfonatopropyl)-2,7-dibromofluorene acid form, diBr-F3SO$_3$H. Upon drying, diBr-F3SO$_3$H (2.47 g, 4.2 mmol) was added into a 150-mL 2-neck rbf, fitted with a stopcock valve adaptor. The rbf was pumped down to vacuum and backfilled with Ar thrice. 80 mL of distilled THF was added to dissolve the monomer. Catalytic dry DMF (0.25 mL) was added, followed by dropwise addition of oxalyl chloride (7.1 mL, 84.0 mmol). The reaction was left to stir at RT for 6 h. Chlorination yield can be monitored by 1H NMR by quenching a small sample extracted from the reaction pot. Upon completion, the unstable 9,9-bis(3'-chlorosulfonylpropyl)-2,7-dibromofluorene intermediate, diBr-F3SO$_2$Cl was dried in-situ with vacuum and re-dissolved in anhydrous chloroform (40 mL).

In a 2nd rbf, trifluoromethanesulfonamide (TFMS, 12.5 g, 84.0 mmol) was mixed with anhydrous triethylamine (TEA, 11.7 mL, 84.0 mmol) in 30 mL of anhydrous chloroform. This mixture was transferred to the diBr-F3SO$_2$Cl solution and left to stir at RT for 1 h. Upon completion, the reaction was precipitated twice in diethyl ether, and redissolved in chloroforom. After the 2nd redissolution in chloroform, the crude product was washed with water and precipitated in diethyl ether, yielding pure **diBr-F3CF$_3$SIS-TEAH** as white solid (4.2 g, Yield = 97%). ^{1}H NMR (400 MHz, DMSO-d$_6$), δ(ppm): 7.82-7.78 (d, 2H), 7.70 (s, 2H), 7.57-7.54 (d, 2H), 3.12-3.07 (q, 12H), 2.74-2.71 (t, 4H), 2.12-2.08 (t, 4H), 1.20-1.16 (t,18H), 0.86-0.81 (m, 4H). ^{19}F NMR (400 MHz, DMSO-d$_6$), δ(ppm): -78.8 (s)

To yield **diBr-F3C$_2$F$_5$SIS-TEAH**, in a 2nd rbf, replace TFMS reagent with pentafluoroethanesulfonamide (PFES) with all other reaction conditions and purification procedures remaining unchanged. Pure **2** is obtained as white solid (Yield = 95%). ^{1}H NMR (400 MHz, DMSO-d$_6$), δ(ppm): 7.82-7.78 (d, 2H), 7.70 (s, 2H), 7.57-7.54 (d, 2H), 3.12-3.07 (q, 12H), 2.74-2.71 (t, 4H), 2.12-2.08 (t, 4H), 1.20-1.16 (t,18H), 0.86-0.81 (m, 4H). ^{19}F NMR (400 MHz, DMSO-d$_6$), δ(ppm): -78.8 (s, 3F), -117.1 (s, 2F)

Synthesis of poly(9,9-bis(3-(trifluoroethanesulfonylimidosulfonyl)propyl)fluorine-2,7-diyl-*alt*-1,4-phenylene-N-(*p*-sec-butylphenylimino)-1,4-phenylene) sodium TFB-CF$_3$SIS-Na, and poly(9,9-bis(3-(trifluoroethanesulfonylimidosulfonyl)propyl)fluorene-2,7-diyl-*alt*-1,4-phenylene-(*m*-trifluoromethylphenylimino)-1,4-phenylene) sodium mTFF-CF$_3$SIS-Na



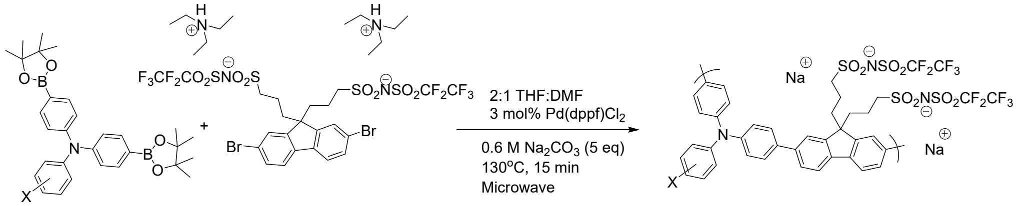
diEs-mTFF/ diEs-TFB **diBr-F3C$_2$F$_5$SIS-TEAH** **mTFF-C$_2$F$_5$SIS-Na/ TFB-C$_2$F$_5$SIS-Na**

In a 20-mL microwave-safe vial, equimolar portion of **diBr-F3CF$_3$SIS-TEAH** (500.00 mg, 0.48 mmol), **diEs-mTFF** (271.3 mg, 0.48 mmol) and catalytic Pd(dppf)Cl$_2$ (11.86 mg, 3 mol%) were added. The vial was crimp-sealed, pumped down to vacuum and backfilled with Ar thrice. 6 mL of 2:1 THF:DMF mixture was added to dissolve the monomers, before addition of 5 eq of 0.6 M Na$_2$CO$_3$ solution (4 mL). The solution was degassed with Ar for 15 min before heating in a microwave at 130^{o}C (15 min). Upon cooling to RT, the polymer was precipitated in water and retrieved by centrifugation. The polymer solids were washed with diethyl ether and collected on a 0.2 µm nylon filter. For removal of Pd^{2+} catalyst residues, the polymer was re-dissolved in acetonitrile and mixed in sodium diethyldithiocarbamate solution, before precipitation in water to yield **mTFF-CF$_3$SIS-Na** as off-white solids. Residual TEAH from monomer **1** is quantified by ^{1}H NMR and removed by mixing the polymer solution in MeOH with equivalent quantities of NaOH with respect to calculated amount of residual TEAH. The polymer is finally purified by dialysis in MeOH through a regenerated cellulose membrane (MWCO = 12-14 kDa) to remove low Mw polymer and other ionic impurities followed by precipitation in diethyl ether and a final water wash of the precipitated polymer solids. ^{1}H NMR (400 MHz, DMSO-d6), δ (ppm): 7.93 – 7.22 (m, 18H), 2.83 – 2.70 (m, 4H), 2.28 – 2.10 (m, 4H), 1.05 – 0.86 (m, 4H). M$_n$ by ^{1}H NMR end-group analysis = 53 kDa.

To yield the TFB polymer variant, replace **diEs-mTFF** with equimolar quantity of **diEs-TFB**, with all other reaction conditions and purification procedures remaining unchanged. Pure **TFB-**

CF_3SIS-Na is obtained as off-white solids as well. ^{1}H NMR (400 MHz, DMSO-d6), δ (ppm): 7.91 – 7.12 (m, 18H), 2.76 – 2.58 (m, 5H), 2.25 – 2.18 (m, 4H), 1.61 – 1.57 (m, 2H), 1.25 – 1.23 (m, 3H), 0.99 – 0.82 (m, 7H). M_n by ^{1}H NMR end-group analysis = 48 kDa.

Synthesis of poly(9,9-bis(3-(pentafluoroethanesulfonylimidosulfonyl)propyl)fluorine-2,7-diyl-*alt*-1,4-phenylene-N-(*p*-sec-butylphenylimino)-1,4-phenylene) sodium TFB-C_2F_5SIS-Na, and poly(9,9-bis(3-(pentafluoroethanesulfonylimidosulfonyl)propyl)fluorene-2,7-diyl-*alt*-1,4-phenylene-(*m*-trifluoromethylphenylimino)-1,4-phenylene) sodium mTFF-C_2F_5SIS-Na



diEs-mTFF/
diEs-TFB

diBr-F3C_2F_5SIS-TEAH

mTFF-C_2F_5SIS-Na/
TFB-C_2F_5SIS-Na

In a 2-mL microwave-safe vial, equimolar portion of **diEs-mTFF** (49.89 mg, 0.088 mmol) and **2** (100 mg, 0.088 mmol) were added, together with catalytic Pd(dppf)Cl_2 (2.16 mg, 3 mol%). The vial was crimp-sealed, pumped down to vacuum and backfilled with Ar thrice. 1.26 mL of 2:1 THF:DMF mixture was added to dissolve the monomers, before addition of 5 eq of 0.66 M Na_2CO_3 solution (0.64 mL). The solution was bubbled with Ar for 15 min before heating in a microwave at 130^{o}C (15 min). Upon cooling to RT, the polymer was precipitated in water and retrieved by centrifugation. The polymer solids were washed with diethyl ether and collected on a 0.2 µm nylon filter. For removal of Pd^{2+} catalyst residues, the polymer was re-dissolved in acetonitrile and mixed in sodium diethyldithiocarbamate solution, before precipitation in water to yield **mTFF-C_2F_5SIS-Na** as off-white solids. Residual TEAH from monomer **diBr-FC_2F_5SIS-TEAH** is quantified by 1H NMR and removed by mixing the polymer solution in MeOH with equivalent quantities of NaOH with respect to calculated amount of residual TEAH. The polymer is purified by dialysis in MeOH through a regenerated cellulose membrane (MWCO = 12-14 kDa) to remove low Mw polymer and other ionic impurities followed by precipitation in diethyl ether and a final water wash of the precipitated polymer solids. ^{1}H NMR (400 MHz, DMSO-d6), δ (ppm): 7.98 – 7.11 (m, 18H), 2.85 – 2.69 (m, 4H), 2.30 – 2.10 (m, 4H), 1.06 – 0.88 (m, 4H). M_n by ^{1}H NMR end-group analysis = 25 kDa.

To yield the **TFB-C_2F_5SIS-Na** polymer, replace **diEs-mTFF** with equimolar quantity of **diEs-TFB**, with all other reaction conditions and purification procedures remaining unchanged. Pure **TFB-C_2F_5SIS-Na** is obtained as off-white solids as well. ^{1}H NMR (400 MHz, DMSO-d6), δ (ppm): 7.87 – 7.07 (m, 18H), 2.76 – 2.56 (m, 5H), 2.25 – 2.18 (m, 4H), 1.61 – 1.57 (m, 2H), 1.25 – 1.23 (m, 3H), 0.99 – 0.82 (m, 7H). M_n by ^{1}H NMR end-group analysis = 23 kDa.

Ion-exchange of Na cation in TFB-X-Na and mTFF-X-Na polymers

In a 100-mL Nalgene bottle, Amberlyst hydrogen form H^+ resins (1.7 molar equvi/mL by wetted bed volume, Sigma-Aldrich Pte Ltd) were conditioned to the tetramethylammonium ($^+NMe_4$) and tetraphenylphosphosium ($^+PPh_4$) cations by addition of 1.5 molar equivalents of their respective tetramethylammonium hydroxide and tetraphenylphosphosium bromide in aqueous solvent and left on a mechanical roller at room temperature for 3 h. The ion-exchanged resins were then rinse-washed with deionized water until pH 7, and pre-conditioned in acetonitrile for 24 h. TFB-CF_3SIS-Na was dissolved in acetonitrile at 50 mg/mL and added to 20 molar equivalents of ion-exchange resins. The mixture was left on a mechanical roller at room temperature for 6 h. The solutions were concentrated and precipitated in diethyl ether. The TFB-CF_3SIS-NMe_4 and TFB-CF_3SIS-PPh_4 polymers are further purified by dialysis in acetonitrile through a regenerated cellulose membrane (MWCO = 12-14 kDa) for 1 h for four times. The dialysed polymers were retrieved by precipitation in diethyl ether and dried under vacuum.

Solvent for undoped TAF polymers

X =	M =	Solubility (>20 mg ml^{-1})						
		DMSO	MeOH	ACN	PC	Acetone	NM	TFE
SO_3	Na	Y	Y	N	N	N	Y	Y
	NMe_4	Y	Y	N	N	N	Y	Y
	PPh_4	Y	Y	Y	Y	Y	Y	Y
C_3FSIS	Na	Y	Y	Y	Y	Y	Y	Y
	NMe_4	Y	Y	Y	Y	Y	Y	Y
C_2F_5SIS	Na	Y	Y	Y	Y	Y	Y	Y

Table 1. Solubility characteristics of TFB-X-M and mTFF-X-M, where M is the cation. Both the TFB and mTFF cores exhibit the same behavior, and are thus not repeated in the table for brevity. M = Na, NMe_4 or PPh_4, where NMe_4 is tetramethylammonium, and PPh_4 is tetraphenylphosphonium. Solubility: Y = Yes, N = No. Solvents: DMSO, dimethyl sulfoxide; ACN, acetonitrile; PC, propylene carbonate; MeOH, methanol; TFE, 2,2,2-trifluoroethanol; NM, nitromethane.

Atomic force microscopy of undoped and *SC* hole-doped TAF polymers

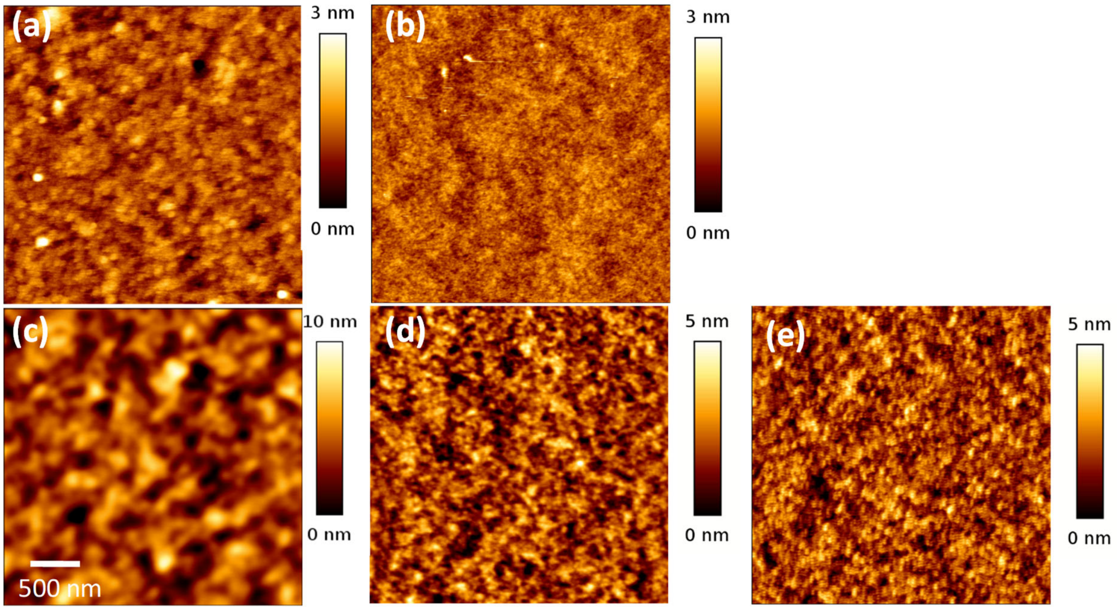


Figure 1. 3x3-μm atomic force microscopy images of pristine and *SC* hole-doped polymers. 90-nm-thick undoped **(a)** TFB-CF_3SIS-Na, **(b)** TFB-C_2F_5SIS-Na. 30-nm-thick *SC* hole-doped **(c)** TFB-CF_3SIS-Na and **(d)** TFB-C_2F_5SIS-Na **(e)** mTFF-C_2F_5SIS-Na films. Undoped films are spin-cast from 20 mM polymer solutions in ACN while *SC* hole-doped films are spin-cast from 15 mM hole-doped solutions in ACN and filtered through 0.45-μm nylon syringe filter onto O_2-plasma cleaned glass substrates. RMS roughness of **(a)** – **(e)** films are 0.34 nm, 0.25 nm, 1.50 nm, 0.77 nm and 0.71 nm respectively. Tapping-mode AFM.

Reference

1. C.G. Tang, M.C.Y. Ang, K.K. Choo, V. Keerthi, J.K. Tan, M. Nur Syafiqah, T. Kugler, J.H. Burroughes, R.Q. Png, L.L. Chua, and P.K.H. Ho, *Nature*, 2016, **539**, 536.