SUPPLEMENTARY INFORMATION (SI)

Fluorination Effects on Indacenodithienothiophene Acceptor Packing and Electronic Structure, End-Group Redistribution, and Solar Cell Photovoltaic Response

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1. Materials and Methods

All reagents were purchased from commercial sources and were used without further purification unless noted otherwise. **ITIC (ITIC-0F)** was purchased from 1-Material Inc.. \( \text{N,N-dimethylformamide}(\text{carbonyl-}1^3\text{C, 99%}) \) was purchased from Cambridge Isotope Laboratories and used as received.

Copolymer molecular weights were determined on a Polymer Laboratories PL-GPC 220 instrument equipped with a set of three PLgel 10 \( \mu \text{m} \) mixed-B columns using 1,2,4-trichlorobenzene (stabilized with 125 ppm of BHT) as eluent at 150 °C and calibrated to polystyrene standards. Copolymer samples were pre-dissolved at ~ 1.00 mg/mL concentration in 1,2,4-trichlorobenzene while shaking for 2 h at 150 °C.

NMR spectra were recorded on Agilent DD MR-400 (FT, 400 MHz, \(^1\text{H}; 101 \text{ MHz, } 1^3\text{C}; 376 \text{ MHz, } 19^\text{F})\), Bruker Avance III (FT, DCH Cryoprobe, 500 MHz, \(^1\text{H}; 126 \text{ MHz, } 1^3\text{C})\), Agilent DD2 (FT, 500 MHz, \(^1\text{H}; 470 \text{ MHz, } 19^\text{F})\), Bruker Neo (FT, QCI-F cryoprobe, 600 MHz, \(^1\text{H}; 151 \text{ MHz, } 1^3\text{C}; 564 \text{ MHz, } 19^\text{F})\) spectrometers at 25 °C unless noted otherwise. NFA NMR samples were prepared at a concentration of 2.0 mg/mL. Chemical shifts for \(^1\text{H} \) and \(^1^3\text{C} \) spectra are referenced to residual protio-solvent signals (\( \delta ^1\text{H} = 7.26 \) for CDCl3, 5.32 for CD2Cl2, 2.50 for (CD3)2SO; \( \delta ^1^3\text{C} = 77.16 \) for CDCl3, 53.84 for CD2Cl2, 39.52 for (CD3)2SO) and chemical shifts are reported in ppm.

HRMS was performed on an Agilent 6210A LC-TOF instrument with ESI ionization in positive ion mode. Samples were prepared in DCM and a direct injection of the sample was performed with a carrier solvent mixture of DCM:MeOH (75:25 v:v).
2. Materials Synthesis and Purification

Scheme S1. Synthesis of the trifluorinated end-group fragment.

1: In an oven-dried 500 mL round bottom flask, 3,4,5-trifluorobenzoic acid (8.80 g, 1.0 equiv, 50 mmol) was dissolved in anhydrous THF (167 mL) under N₂-atmosphere and then cooled to –78 °C. n-BuLi [Caution! Pyrophoric!] (2.71 M in hexanes, 40.6 mL, 2.2 equiv, 110 mmol) was added dropwise and then stirred for 3 h at –78 °C. Dry CO₂ gas was then bubbled through the solution until it formed a thick slurry and then the mixture was allowed to warm to r.t. slowly overnight. The mixture was next poured into H₂O (500 mL), acidified with 2M HCl (80 mL), and then extracted with EtOAc (3 × 250 mL). The organic layer was dried over Na₂SO₄, filtered, and then concentrated under reduced pressure. The dried solid was dissolved in a minimum volume of EtOAc and then dripped into hexanes (200 mL) and cooled to –20 °C. The product was collected by filtration and then dried under high vacuum (<30 mTorr) at 60 °C for 12 h and obtained as an off-white solid (9.82 g, 44.6 mmol, 89%).

1H NMR (400 MHz, (CD₃)₂SO) δ 13.90 (s, 2H), 7.79 (ddd, JH–F = 10.3, 6.9, 2.0 Hz, 1H). 19F NMR (376 MHz, (CD₃)₂SO) δ -132.20 (ddd, JF–F = 21.8, 7.5 Hz, JF–H = 10.3 Hz, 1F), -137.45 (ddd, JF–F = 22.0, 7.5 Hz, JF–H = 1.8 Hz, 1F), -153.63 (td, JF–F = 21.9, JF–H = 7.0 Hz, 1F). 13C NMR (126 MHz, (CD₃)₂SO) δ 164.5, 163.7, 150.8, 150.8, 150.7, 150.7, 148.8, 148.8, 148.7, 148.3, 148.2, 146.4, 146.3, 146.3, 146.2, 142.4, 142.3, 142.2, 140.4, 140.2, 140.1, 125.5, 125.5, 125.5, 122.7, 122.7, 122.6, 122.6, 114.6, 114.6, 114.5, 114.4.

2: 1 (10.51 g, 1.0 equiv, 47.8 mmol) was dissolved in Ac₂O (48 mL) under N₂-atmosphere and heated at 140 °C for 20 h. The mixture was cooled and then concentrated under reduced pressure. The product was obtained as an off-white waxy solid and used without further purification (8.76 g, 43.4 mmol, 91%).

1H NMR (400 MHz, (CD₃)₂SO) δ 8.31 (ddd, JH–F = 7.8, 5.7, 1.5 Hz, 1H). 19F NMR (376 MHz, (CD₃)₂SO) δ -119.12 (ddd, JF–F = 19.3, 13.7 Hz, JF–H = 8.0 Hz, 1F), -132.49 (ddd, JF–F = 21.5, 14.0 Hz, JF–H = 1.2 Hz, 1F), -147.75 (ddd, JF–F = 21.1, 19.4, JF–H = 5.7 Hz, 1F). 13C NMR (126 MHz, (CD₃)₂SO) δ 160.8, 158.1, 156.7, 156.6, 154.6, 154.5, 147.4, 147.3, 145.3, 145.2, 145.1, 145.0, 145.0, 144.9, 143.0, 142.9, 142.9, 142.8, 127.7, 127.7, 116.6, 116.5, 111.6, 111.6, 111.4, 111.4.
3: In an oven-dried 100 mL Schlenk flask, 2 (6.06 g, 1.0 equiv, 30.0 mmol) was dissolved in Ac₂O (30 mL) under N₂-atmosphere. Then, tert-butyl acetoacetate (5.22 g, 1.1 equiv, 33.0 mmol) and triethylamine (15 mL) were added. The solution was stirred at room temperature for 12 h. The solution was then poured into a mixture of H₂O (60 mL), conc. HCl (60 mL), and ice (~60 g) at 0 °C. The resulting mixture was stirred for 30 min. at 0 °C, diluted with 2M HCl (300 mL), and then heated at 80 °C for 2 h under a flow of N₂ gas. The solution was cooled and then extracted with DCM (3 × 150 mL). The organic layer was dried over Na₂SO₄, filtered, and then concentrated under reduced pressure. The product was purified by sublimation (60 °C, 25 mTorr) for 24 h and obtained as a white/pink crystalline solid (2.04 g, 10.2 mmol, 34%).

1H NMR (400 MHz, CDCl₃) δ 7.60 (ddd, J_H–F = 7.4, 5.7, 1.7 Hz, 1H), 3.29 (s, 2H). 19F NMR (376 MHz, CDCl₃) δ -116.91 (ddd, J_F–F = 18.3, 14.8 Hz, J_F–H = 7.4 Hz, 1F), -130.66 (ddd, J_F–F = 19.5, 14.8, J_F–H = 1.7 Hz, 1F), -146.20 (ddd, J_F–F = 19.5, 18.5, J_F–H = 5.8 Hz, 1F). 13C NMR (126 MHz, CDCl₃) δ 193.9, 191.4, 157.7, 157.7, 157.6, 156.5, 155.6, 155.5, 148.1, 148.1, 148.0, 146.3, 146.2, 146.1, 146.1, 146.0, 146.0, 145.9, 145.9, 145.9, 144.2, 144.1, 144.0, 138.8, 138.8, 138.8, 128.0, 127.9, 127.9, 127.9, 107.8, 107.8, 107.7, 107.6, 45.2.

2-(4,5,6-trifluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (4): In an oven-dried 100 mL Schlenk flask, 3 (2.00 g, 1.0 equiv, 10.0 mmol) and malononitrile (1.32 g, 2.0 equiv, 20.0 mmol) were dissolved in anhydrous EtOH (20 mL) under N₂-atmosphere and stirred for 15 min. Then, anhydrous NaOAc (1.07g, 1.3 equiv, 13.0 mmol) was added and the solution was stirred for 30 min. H₂O (40 mL) was added to the solution and then 2M HCl (~10 mL) was then added dropwise until a gray precipitate formed. The precipitate was filtered and then purified by sublimation (115 °C, 25 mTorr) for 12 h. The sublimed material was dissolved in DCM (10 mL) and then dripped into hexanes (100 mL). The solution was cooled to –78 °C. The resulting brown precipitate was filtered and then re-precipitated into hexanes following the above protocol. The re-filtered product then was dried under high vacuum (~<25 mTorr) at room temperature for 12 h and obtained as a brown solid (360 mg, 1.45 mmol, 15%).

1H NMR (500 MHz, CDCl₃) δ 8.32 (ddd, J_H–F = 8.7, 5.6, 1.7 Hz, 1H), 3.79 (s, 2H). 19F NMR (470 MHz, CDCl₃) δ -115.46 (ddd, J_F–F = 18.6, 15.6 Hz, J_F–H = 8.8 Hz, 1F), -131.11 (ddd, J_F–F = 20.5, 15.7 Hz, J_F–H = 1.4 Hz, 1F), -144.23 (ddd, J_F–F = 20.5, 19.0 Hz, J_F–H = 5.6 Hz, 1F). 13C NMR (126 MHz, CDCl₃) δ 189.2, 163.0, 163.0, 157.4, 157.3, 157.3, 157.2, 155.2, 155.2, 155.2, 155.1, 148.8, 148.8, 148.7, 148.7, 148.6, 146.6, 146.6, 146.5, 146.5, 145.4, 145.3, 145.3, 145.2, 143.3, 143.2, 143.2, 143.0, 137.8, 137.8, 137.8, 137.8, 137.8, 137.7, 137.7, 125.8, 125.8, 125.8, 125.7, 125.7, 111.5, 111.4, 110.9, 110.9, 110.8, 81.5, 81.5, 43.9.
Scheme S2. Synthesis of the ITIC-nF NFAs.

6,6,12,12-Tetrakis(4-hexylphenyl)-6,12-dihydridithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene-2,8-dicarboxaldehyde (5): 5 was purchased from Sunatech and used as received. The NMR spectroscopic data are in good agreement with those previously reported.1

1H NMR (400 MHz, CD2Cl2) δ 9.88 (s, 2H), 7.98 (s, 2H), 7.67 (s, 2H), 7.16 (d, J = 8.5 Hz, 8H), 7.12 (d, J = 8.5 Hz, 8H), 2.75 – 2.37 (m, 8H), 1.57 (p, J = 7.5 Hz, 8H), 1.38 – 1.21 (m, 24H), 1.05 – 0.65 (m, 12H).

2-(3-oxo-indan-1-ylidene)-malononitrile (6): 6 was prepared following reported procedures.2 The NMR spectroscopic data are in good agreement with those previously reported.

1H NMR (400 MHz, CDCl3) δ 8.66 (d, J = 7.8 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.90 (td, J = 7.6, 1.4 Hz, 1H), 7.85 (td, J = 7.4, 0.9 Hz, 1H), 3.73 (s, 2H).

2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (7): 7 was purchased from Sunatech and additionally purified via sublimation (100 °C, 30 mTorr). The NMR spectroscopic data are in good agreement with those previously reported.3

1H NMR (400 MHz, CDCl3) δ 8.47 (dd, J = 9.3, 6.5 Hz, 1H), 7.76 (dd, J = 7.6, 7.3 Hz, 1H), 3.76 (s, 2H). 19F NMR (376 MHz, CDCl3) δ -119.40 (ddd, J = 19.0, 9.2, 7.2 Hz, 1F), -119.87 (ddd, J = 19.0, 7.7, 6.7 Hz, 1F).
In an oven-dried 50 mL round bottom flask equipped with reflux condenser, 5 (215.1 mg, 1.0 equiv, 0.20 mmol) and 6 (38.8 mg, 1.0 equiv, 0.20 mmol) were dissolved in a mixture of anhydrous CHCl₃ (20 mL) and anhydrous pyridine (0.5 mL) under N₂-atmosphere. The reaction mixture was heated at reflux for 16 h. The reaction mixture was then cooled to r.t. and concentrated under reduced pressure. The residue was purified by four sequential rounds of column chromatography (SiO₂: toluene). The blue band with intermediate \( R_f \) is the target product. The product was dissolved in DCM (5 mL) then precipitated into MeOH (100 mL), filtered, and dried under vacuum (<30 mTorr) at 50 °C for 24 h. The product was obtained as a dark solid (98.8 mg, 0.079 mmol, 39%).

**1H NMR** (500 MHz, CD₂Cl₂) \( \delta \) 9.89 (s, 1H), 8.85 (s, 1H), 8.67 (d, \( J = 7.5 \) Hz, 1H), 8.22 (s, 1H), 7.99 (s, 1H), 7.93 – 7.87 (m, 1H), 7.79 (td, \( J = 7.6, 1.5 \) Hz, 1H), 7.75 (td, \( J = 7.4, 1.0 \) Hz, 1H), 7.71 (s, 1H), 7.68 (s, 1H), 7.23 (d, \( J = 8.3 \) Hz, 4H), 7.20 – 7.03 (m, 12H), 2.67 – 2.46 (m, 8H), 1.65 – 1.53 (m, 8H), 1.40 – 1.17 (m, 24H), 0.94 – 0.77 (m, 12H). **13C NMR** (126 MHz, CD₂Cl₂) \( \delta \) 188.4, 183.2, 160.8, 155.9, 155.2, 153.2, 149.7, 147.6, 147.4, 146.9, 145.1, 143.9, 143.1, 143.0, 142.8, 140.5, 140.0, 139.6, 139.5, 138.3, 137.6, 137.3, 137.1, 136.6, 135.6, 134.9, 130.4, 129.2, 128.3, 128.2, 125.6, 124.0, 123.4, 118.9, 118.5, 115.1, 115.0, 70.0, 63.6, 63.6, 35.9, 35.9, 32.1, 31.8, 29.6, 29.5, 23.0, 14.2. HRMS: Calcd for \([ C_{82}H_{78}N_{2}O_{2}S_{4} + H]^{+}\), m/z = 1251.5019. Found: m/z = 1251.5008 \([M+H]^{+}\).

**ITIC-2F:** In an oven-dried 50 mL round bottom flask equipped with reflux condenser, 5 (107.6 mg, 1.0 equiv, 0.10 mmol), 6 (23.3 mg, 1.2 equiv, 0.12 mmol), and 7 (27.6 mg, 1.2 equiv, 0.12 mmol) were dissolved in a mixture of anhydrous CHCl₃ (30 mL) and anhydrous pyridine (0.6 mL) under N₂-atmosphere. The reaction mixture was heated at reflux for 16 h. The reaction mixture was then cooled to r.t. and concentrated under reduced pressure. The residue was purified by four sequential rounds of column chromatography (SiO₂: toluene). The blue band with intermediate \( R_f \) is the target product. The product was dissolved in DCM (5 mL) then precipitated into hexanes (100 mL) at –20 °C, filtered, and dried under vacuum (<30 mTorr) at 50 °C for 24 h. The product was obtained as a dark solid (31.6 mg, 0.022 mmol, 22%).

Note: **ITIC-2F** can also be synthesized from 8 (93.9 mg, 1.0 equiv, 0.075 mmol) and 7 (25.9 mg, 1.5 equiv, 0.113 mmol) under similar reaction conditions and purification procedures (16.5 mg, 0.011 mmol, 15%).

**1H NMR** (500 MHz, CD₂Cl₂) \( \delta \) 8.85 (s, 1H), 8.84 (s, 1H), 8.67 (d, \( J = 7.7 \) Hz, 1H), 8.52 (dd, \( J_{H-H} = 10.1, 6.5 \) Hz, 1H), 8.24 (s, 1H), 8.22 (s, 1H), 7.93 – 7.88 (m, 1H), 7.80 (dd, \( J = 7.5, 1.5 \) Hz, 1H), 7.76 (td, \( J = 7.3, 0.9 \) Hz, 1H), 7.72 (s, 1H), 7.23 (d, \( J = 7.6 \) Hz, 8H), 2.65 – 2.49 (m, 8H), 1.58 (p, \( J = 7.9, 7.4 \) Hz, 8H), 1.40 – 1.20 (m, 24H), 0.92 – 0.79 (m, 12H). **19F NMR** (470 MHz, CD₂Cl₂) \( \delta \) -123.98 (ddd, \( J_{F-F} = 17.7 \) Hz, \( J_{F-H} = 9.9, 7.6 \) Hz, 1F), -125.11 (dt, \( J_{F-F} = 19.0 \) Hz, \( J_{F-H} = 7.3 \) Hz, 1F). **13C NMR** (126 MHz, CD₂Cl₂) \( \delta \) 188.4, 186.1, 160.7, 158.7, 156.2, 156.1, 153.9, 153.9, 153.9, 153.8, 152.8, 148.1, 147.9, 147.4, 146.7, 144.4, 144.2, 143.2, 143.1, 140.5, 139.9, 139.6, 139.3, 138.6, 138.3, 137.7, 137.6, 137.3, 137.2, 137.1, 137.0, 135.6, 135.1, 135.0, 134.9, 129.2, 128.3, 128.3, 125.6, 125.3, 124.1, 123.7, 122.5, 119.0, 118.9, 115.3, 115.2, 115.1, 115.0, 114.7, 114.6, 113.1, 112.9,
70.5, 70.1, 63.6, 35.9, 32.1, 31.8, 29.5, 23.0, 14.2. HRMS: Calcd for [C₉₄H₈₀F₂N₄O₂S₄ + H]⁺, m/z = 1464.5238. Found: m/z = 1464.5190 [M+H]⁺.

**ITIC-6F:** In an oven-dried 50 mL round bottom flask equipped with reflux condenser, 5 (322.7 mg, 1.0 equiv, 0.30 mmol) and 4 (186.1 mg, 2.5 equiv, 0.75 mmol) were dissolved in a mixture of anhydrous CHCl₃ (90 mL) and anhydrous pyridine (1.8 mL) under N₂-atmosphere. The reaction mixture was heated at reflux for 16 h. The reaction mixture was then cooled to r.t. and concentrated under reduced pressure. The residue was purified by three sequential rounds of column chromatography (SiO₂: chlorobenzene). The product was dissolved in DCM (10 mL) then precipitated into hexanes (150 mL) at −20 °C, filtered, and dried under vacuum (<30 mTorr) at 50 °C for 24 h. The product was obtained as a dark solid (220.2 mg, 0.143 mmol, 48%).

1H NMR (500 MHz, CD₂Cl₂) δ 8.87 (s, 2H), 8.38 (dd, JHF = 9.4, 5.3 Hz, 2H), 8.23 (s, 2H), 7.73 (s, 2H), 7.22 (d, J = 8.4 Hz, 8H), 7.16 (d, J = 8.4 Hz, 8H), 2.64 – 2.51 (m, 8H), 1.58 (p, J = 7.7 Hz, 8H), 1.41 – 1.21 (m, 24H), 0.93 – 0.79 (m, 12H). 19F NMR (470 MHz, CD₂Cl₂) δ -120.31 (ddd, JF-F = 18.9, 13.0 Hz, JF-H = 9.9 Hz, 2F), -136.49 (dd, JF-F = 20.4, 13.4 Hz, 2F), -149.20 (td, JF-F = 20.0 Hz, JF-H = 5.4 Hz, 2F). 13C NMR (126 MHz, CD₂Cl₂) δ 183.7, 157.7, 156.4, 154.4, 148.2, 144.6, 143.2, 139.7, 139.3, 139.1, 138.5, 137.5, 136.0, 135.9, 129.2, 128.2, 121.9, 121.8, 119.2, 114.6, 114.4, 111.1, 111.0, 71.1, 63.6, 35.9, 32.1, 31.8, 29.5, 23.0, 14.2. HRMS: Calcd for [C₉₄H₇₆F₆N₄O₂S₄ + H]⁺, m/z = 1536.4862. Found: m/z = 1536.4814 [M+H]⁺.

**ITIC-3F:** In an oven-dried 50 mL round bottom flask equipped with reflux condenser, ITIC-6F (159.3 mg, 1.0 equiv, 0.1 mmol) and 6 (25.2 mg, 1.25 equiv, 0.13 mmol) were dissolved in a mixture of anhydrous CHCl₃ (30 mL) and anhydrous pyridine (0.6 mL) under N₂-atmosphere. The reaction mixture was heated at reflux for 18 h. The reaction mixture was then cooled to r.t. and concentrated under reduced pressure. The residue was purified by three sequential rounds of column chromatography with SiO₂: chlorobenzene and once with SiO₂: toluene. The product was dissolved in DCM (5 mL) then precipitated into hexanes (100 mL) at −20 °C, filtered, and dried under vacuum (<30 mTorr) at 50 °C for 24 h. The product was obtained as a dark solid (46.7 mg, 0.032 mmol, 30%).

1H NMR (500 MHz, CD₂Cl₂) δ 8.87 (s, 1H), 8.85 (s, 1H), 8.67 (d, J = 7.6 Hz, 1H), 8.38 (dd, JHF = 9.5, 5.3 Hz, 1H), 8.23 (s, 2H), 7.95 – 7.86 (m, 1H), 7.75 (td, J = 7.6, 1.6 Hz, 1H), 7.76 (td, J = 7.4, 1.0 Hz, 1H), 7.73 (s, 1H), 7.29 – 7.20 (m, 8H), 7.16 (d, J = 8.4 Hz, 8H), 2.63 – 2.50 (m, 8H), 1.58 (p, J = 7.7 Hz, 8H), 1.41 – 1.21 (m, 24H), 0.92 – 0.79 (m, 12H). 19F NMR (470 MHz, CD₂Cl₂) δ -120.39 (ddd, JF-F = 18.9, 12.9 Hz, JF-H = 10.0 Hz, 1F), -136.54 (dd, JF-F = 20.3, 13.4 Hz, 1F), -149.26 (td, JF-F = 19.9 Hz, JF-H = 5.4 Hz, 1F). 13C NMR (126 MHz, CD₂Cl₂) δ 188.4, 183.7, 160.7, 157.7, 156.4, 156.1, 154.7, 152.7, 148.3, 148.2, 148.0, 146.6, 144.5, 144.3, 143.2, 143.1, 140.5, 140.0, 139.6, 139.3, 139.1, 138.5, 137.5, 136.0, 135.9, 129.2, 128.6, 138.3, 137.8, 137.3, 137.0, 135.6, 134.9, 129.2, 129.2, 128.3, 128.2, 125.6, 125.3, 124.1, 123.7, 121.8, 119.1, 118.9, 115.1, 115.0, 114.6, 114.5, 111.1, 110.9, 71.0, 70.2, 63.6, 63.6, 35.9, 32.1, 31.8, 29.6, 23.0, 14.2. HRMS: Calcd for [C₉₄H₇₆F₃N₄O₂S₄ + H]⁺, m/z = 1482.5144. Found: m/z = 1482.5035 [M+H]⁺.
**ITIC-4F**: ITIC-4F was purchased from 1-Material Inc. and additionally purified by column chromatography (SiO$_2$: chlorobenzene). The isolated NFA was dissolved in DCM (5 mL) then precipitated into hexanes (100 mL) at –20 °C, filtered, and dried under vacuum (<30 mTorr) at 50 °C for 24 h. The NMR spectroscopic data are in good agreement with those previously reported.\(^4\)

$^1$H NMR (500 MHz, CD$_2$Cl$_2$) $\delta$ 8.84 (s, 2H), 8.52 (dd, $J_{H-F} = 10.1$, 6.5 Hz, 2H), 8.24 (s, 2H), 7.72 (s, 2H), 7.69 (t, $J_{H-F} = 7.6$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 8H), 7.16 (d, $J = 8.4$ Hz, 8H), 2.66 – 2.49 (m, 8H), 1.58 (p, $J = 7.7$ Hz, 8H), 1.41 – 1.19 (m, 24H), 0.94 – 0.79 (m, 12H). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$) $\delta$ -123.93 (ddd, $J_{F-F} = 17.7$ Hz, $J_{F-H} = 9.9$, 7.6 Hz, 2F), -125.06 (dt, $J_{F-F} = 19.0$, $J_{F-H} = 7.3$ Hz, 2F). HRMS: Calcd for [C$_{94}$H$_{78}$F$_4$N$_4$O$_2$S$_4$ + H]$^+$, m/z = 1500.5050. Found: m/z = 1500.4974 [M+H]$^+$. 

S9
Scheme S3. Synthesis of $^{13}$C-labeled \textit{ITIC-nF} model substrates.

\textbf{9:} $^{1}$ \textit{ITIC-nF} was prepared following modified reported procedures.\textsuperscript{6} The NMR spectroscopic data are in good agreement with those previously reported.\textsuperscript{5}

$^{1}$H NMR (500 MHz, CD$_{2}$Cl$_{2}$) δ 7.54 (s, 2H), 7.31 (s, 4H), 7.17 (d, $J$ = 8.2 Hz, 8H), 7.10 (d, $J$ = 8.2 Hz, 8H), 2.61 – 2.49 (m, 8H), 1.57 (p, $J$ = 7.5 Hz, 8H), 1.38 – 1.20 (m, 24H), 0.91 – 0.80 (m, 12H).

\textbf{10:} In an oven-dried 200 mL Schlenk flask, $^{1}$ \textit{ITIC-nF} (2.04 g, 1.0 equiv, 2.0 mmol) was dissolved in anhydrous THF (80 mL) under N$_{2}$-atmosphere and then cooled to −78 °C. \textit{n}-BuLi [Caution! Pyrophoric!] (2.71 M in hexanes, 1.62 mL, 2.2 equiv, 4.4 mmol) was added dropwise and then stirred for 15 min. at −78 °C. The solution was removed from the cooling bath, allowed to warm to r.t. over the course of 1 h., and then cooled to −78 °C. $N,N$-Dimethylformamide(carbonyl-$^{13}$C) (470 µL, 450 mg, 3.0 equiv, 6.0 mmol) was added dropwise and the solution was warmed to r.t. slowly overnight. The solution was poured into brine (250 mL) and then extracted with CHCl$_{3}$ (3 × 150 mL). The organic layer was dried over Na$_{2}$SO$_{4}$, filtered, and then concentrated under reduced pressure. The residue was purified by column chromatography (SiO$_{2}$: hexanes:DCM
8:2 → 3:7). The product was dissolved in DCM and then precipitated into hexanes (200 mL) and then filtered. The product was dried under vacuum (<20 mTorr) at 60 °C for 12 h and obtained as a goldenrod solid (1.61 g, 1.49 mmol, 75%).

1H NMR (500 MHz, CD2Cl2) δ 9.88 (d, JH–C = 178.6 Hz, 2H), 7.97 (d, JH–C = 3.6 Hz, 2H), 7.68 (s, 2H), 7.17 (d, J = 8.4 Hz, 8H), 7.12 (d, J = 8.3 Hz, 8H), 2.65 – 2.46 (m, 8H), 1.57 (p, J = 7.4 Hz, 8H), 1.38 – 1.22 (m, 24H), 0.92 – 0.79 (m, 12H). 13C NMR (126 MHz, CD2Cl2) δ 183.2 (strong), 155.1, 149.8, 147.0, 144.9 (d, JC–C = 59.9 Hz), 142.9, 142.5 (d, JC–C = 6.6 Hz), 140.1 (d, JC–C = 1.4 Hz), 139.6, 136.9, 130.5 (d, JC–C = 6.1 Hz), 129.1, 128.2, 118.4, 63.6, 35.9, 32.1, 31.8, 29.5, 23.0, 14.3. HRMS: Calcd for [C6813C2H74O2S4 + H]+, m/z = 1077.4712. Found: m/z = 1077.4696 [M+H]+.

13CHO-IDTT(13C)-0F and ITIC(13C)-0F: In an oven-dried 50 mL round bottom flask equipped with reflux condenser, 10 (215.5 mg, 1.0 equiv, 0.20 mmol) and 6 (38.8 mg, 1.0 equiv, 0.20 mmol) were dissolved in a mixture of anhydrous CHCl3 (20 mL) and anhydrous pyridine (0.5 mL) under N2-atmosphere. The reaction mixture was heated at reflux for 16 h. The reaction mixture was then cooled to r.t. and concentrated under reduced pressure. The residue was purified by four sequential rounds of column chromatography (SiO2:toluene). The blue band with intermediate Rf is 13CHO-IDTT(13C)-0F and the blue band with greater Rf is ITIC(13C)-0F. Once purified, the products were dissolved in DCM (5 mL) then precipitated into MeOH (100 mL), filtered, and dried under vacuum (<25 mTorr) at 50 °C for 24 h. Both products were obtained as dark solids (13CHO-IDTT(13C)-0F: 87.8 mg, 0.070 mmol, 35%; ITIC(13C)-0F: 52.5 mg, 0.037 mmol, 18%).

13CHO-IDTT(13C)-0F: 1H NMR (600 MHz, CD2Cl2) δ 9.88 (d, JH–C = 178.6 Hz, 1H), 8.85 (d, JH–C = 151.9 Hz, 1H), 8.67 (d, J = 7.7 Hz, 1H), 8.22 (d, JH–C = 4.1 Hz, 1H), 7.99 (d, JH–C = 3.7 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.79 (td, J = 7.6, 1.4 Hz, 1H), 7.75 (td, J = 7.4, 0.9 Hz, 1H), 7.70 (s, 1H), 7.68 (s, 1H), 7.23 (d, J = 8.4 Hz, 4H), 7.18 – 7.14 (m, 8H), 7.12 (d, J = 8.4 Hz, 4H), 2.63 – 2.52 (m, 8H), 1.63 – 1.54 (m, 8H), 1.37 – 1.22 (m, 24H), 0.90 – 0.81 (m, 12H). 13C NMR (126 MHz, CD2Cl2) δ 188.4, 183.2 (strong), 160.8, 155.9, 155.2, 153.2, 149.7, 147.6, 147.4, 146.9, 145.1 (d, JC–C = 59.7 Hz), 143.9 (d, JC–C = 6.5 Hz), 143.1, 143.0, 142.8 (d, JC–C = 6.5 Hz), 140.5 (d, JC–C = 3.8 Hz), 140.0, 139.9, 139.5, 139.5, 139.4, 138.3 (strong), 137.6, 137.3 (d, JC–C = 2.7 Hz), 137.1 (d, JC–C = 3.8 Hz), 136.6, 135.6, 134.9, 130.4 (d, JC–C = 5.7 Hz), 129.2, 128.3, 128.2, 125.6, 125.3, 124.0, 123.4 (d, JC–C = 72.5 Hz), 118.9, 118.5, 115.1, 115.0, 70.0, 70.0, 63.6, 63.6, 35.9, 35.9, 32.1, 31.8, 29.6, 29.5, 23.0, 14.2. HRMS: Calcd for [C8013C2H78N2O2S4 + H]+, m/z = 1253.5086. Found: m/z = 1253.5079 [M+H]+.

ITIC(13C)-0F: 1H NMR (600 MHz, CD2Cl2) δ 8.85 (d, JH–C = 151.8 Hz, 2H), 8.67 (d, J = 7.7 Hz, 2H), 8.22 (d, JH–C = 4.1 Hz, 2H), 7.92 – 7.88 (m, 2H), 7.79 (td, J = 7.6, 1.4 Hz, 2H), 7.75 (td, J = 7.4, 1.0 Hz, 2H), 7.71 (s, 2H), 7.23 (d, J = 8.4 Hz, 8H), 7.16 (d, J = 8.5 Hz, 8H), 2.62 – 2.52 (m, 8H), 1.64 – 1.55 (m, 8H), 1.39 – 1.22 (m, 24H), 0.91 – 0.80 (m, 12H). 13C NMR (126 MHz, CD2Cl2) δ 188.4, 160.8, 156.1, 152.9, 148.0, 146.8, 144.2, 144.1, 143.1, 140.5, 140.5, 140.2, 139.6, 139.4, 138.6, 138.5, 138.3 (strong), 138.0, 137.3, 137.1, 137.1, 135.6, 134.9, 129.2, 128.3, 125.6, 124.1, 123.8, 123.3, 118.9, 115.1, 115.0, 70.1, 63.6, 35.9, 32.1, 31.8, 29.6, 23.0, 14.2. HRMS: Calcd for [C9213C2H82N4O2S4 + H]+, m/z = 1429.5460. Found: m/z = 1429.5426 [M+H]+.
$^{13}$CHO-IDTT($^{13}$C)-2F and ITIC($^{13}$C)-4F: In an oven-dried 50 mL round bottom flask equipped with reflux condenser, 10 (215.5 mg, 1.0 equiv, 0.20 mmol) and 7 (46.0 mg, 1.0 equiv, 0.20 mmol) were dissolved in a mixture of anhydrous CHCl$_3$ (20 mL) and anhydrous pyridine (0.5 mL) under N$_2$-atmosphere. The reaction mixture was heated at reflux for 16 h. The reaction mixture was then cooled to r.t. and concentrated under reduced pressure. The residue was purified by four sequential rounds of column chromatography (SiO$_2$:toluene). The blue band with intermediate $R_f$ is $^{13}$CHO-IDTT($^{13}$C)-2F and the blue band with greater $R_f$ is ITIC($^{13}$C)-4F. Once purified, the products were dissolved in DCM (5 mL) then precipitated into MeOH (100 mL), filtered, and dried under vacuum (<25 mTorr) at 50 °C for 24 h. Both products were obtained as dark solids ($^{13}$CHO-IDTT($^{13}$C)-2F: 100.3 mg, 0.078 mmol, 39%; ITIC($^{13}$C)-4F: 55.1 mg, 0.037 mmol, 18%).

$^{13}$CHO-IDTT($^{13}$C)-2F: $^1$H NMR (600 MHz, CD$_2$Cl$_2$) $\delta$ 8.85 (d, $J_{H-C} = 151.9$ Hz, 1H), 8.84 (d, $J_{H-F} = 19.0$ Hz, 2H), 8.52 (d, $J_{H-C} = 3.9$ Hz, 1H), 7.99 (d, $J_{H-C} = 3.9$ Hz, 1H), 7.97 (d, $J_{H-C} = 3.9$ Hz, 1H), 7.71 (s, 1H), 7.70 – 7.65 (m, 2H), 7.22 (d, $J = 8.4$ Hz, 4H), 7.18 – 7.14 (m, 8H), 7.12 (d, $J = 8.4$ Hz, 4H), 2.62 – 2.53 (m, 8H), 1.62 – 1.55 (m, 8H), 1.40 – 1.22 (m, 24H), 0.89 – 0.81 (m, 12H). $^{19}$F$\{^1$H$\}$ NMR (564 MHz, CD$_2$Cl$_2$) $\delta$ -123.93 (d, $J_{F-F} = 19.2$ Hz, 2F), -125.06 (d, $J_{F-F} = 19.2$ Hz, 2F). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) $\delta$ 186.1, 158.6, 156.2, 156.0, 155.9, 155.8, 155.8, 155.3, 154.1, 153.9, 153.7, 149.6, 147.5, 145.4, 145.0, 144.2, 144.1, 143.1, 143.0, 142.9, 142.8, 140.0, 139.8, 139.5, 139.4, 139.3, 138.6 (strong), 138.3, 138.3, 137.9, 137.8, 137.8, 136.4, 135.0, 130.4, 130.4, 129.2, 129.2, 128.3, 128.2, 125.3, 122.6, 122.1, 119.0, 118.5, 115.3, 115.2, 114.8, 114.6, 113.0, 112.9, 70.4, 63.6, 63.6, 35.9, 35.9, 32.1, 31.8, 29.5, 29.5, 23.0, 14.2. HRMS: Calcd for [C$_{80}$H$_{76}$F$_2$N$_2$O$_2$S$_4$ + H]$^+$, m/z = 1289.4898. Found: m/z = 1289.4890 [M+H]$^+$. ITIC($^{13}$C)-4F: $^1$H NMR (600 MHz, CD$_2$Cl$_2$) $\delta$ 8.84 (d, $J_{H-C} = 151.9$ Hz, 1H), 8.84 (d, $J_{H-C} = 151.8$ Hz, 1H), 8.67 (d, $J = 7.7$ Hz, 1H), 8.52 (dd, $J_{H-F} = 10.0$, 6.5 Hz, 1H), 8.24 (d, $J_{H-C} = 3.8$ Hz, 1H), 8.24 (d, $J_{H-C} = 3.8$ Hz, 1H), 7.71 (s, 1H), 7.70 – 7.65 (m, 2H), 7.22 (d, $J = 8.4$ Hz, 4H), 7.18 – 7.14 (m, 8H), 7.12 (d, $J = 8.4$ Hz, 4H), 2.62 – 2.53 (m, 8H), 1.62 – 1.55 (m, 8H), 1.40 – 1.22 (m, 24H), 0.89 – 0.81 (m, 12H). $^{19}$F$\{^1$H$\}$ NMR (564 MHz, CD$_2$Cl$_2$) $\delta$ -123.93 (d, $J_{F-F} = 19.2$ Hz, 2F), -125.06 (d, $J_{F-F} = 19.2$ Hz, 2F). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) $\delta$ 186.1, 158.6, 156.2, 156.0, 155.9, 155.8, 155.8, 155.3, 154.1, 153.9, 153.7, 149.6, 147.5, 145.4, 145.0, 144.2, 144.1, 143.1, 143.0, 142.9, 142.8, 140.0, 139.8, 139.5, 139.4, 139.3, 138.6 (strong), 138.3, 138.3, 137.9, 137.8, 137.8, 136.4, 135.0, 130.4, 130.4, 129.2, 129.2, 128.3, 128.2, 125.3, 122.6, 122.1, 119.0, 118.5, 115.3, 115.2, 114.8, 114.6, 113.0, 112.9, 70.4, 63.6, 63.6, 35.9, 35.9, 32.1, 31.8, 29.5, 29.5, 23.0, 14.2. HRMS: Calcd for [C$_{92}$H$_{78}$F$_4$N$_4$O$_2$S$_4$ + H]$^+$, m/z = 1501.5084. Found: m/z = 1501.5019 [M+H]$^+$. ITIC($^{13}$C)-2F: In an oven-dried 50 mL round bottom flask equipped with reflux condenser, 10 (215.5 mg, 1.0 equiv, 0.20 mmol), 6 (46.6 mg, 1.2 equiv, 0.24 mmol), and 7 (55.2 mg, 1.2 equiv, 0.24 mmol) were dissolved in a mixture of anhydrous CHCl$_3$ (20 mL) and anhydrous pyridine (0.5 mL) under N$_2$-atmosphere. The reaction mixture was heated at reflux for 16 h. The reaction mixture was then cooled to r.t. and concentrated under reduced pressure. The residue was purified by four sequential rounds of column chromatography (SiO$_2$:toluene). The blue band with intermediate $R_f$ is ITIC($^{13}$C)-2F. Once precipitated into MeOH (150 mL), filtered, and dried under vacuum (<30 mTorr) at 50 °C for 24 h. The product was obtained as a dark solid (86.4 mg, 0.059 mmol, 29%).

$^1$H NMR (600 MHz, CD$_2$Cl$_2$) $\delta$ 8.85 (d, $J_{H-C} = 151.9$ Hz, 1H), 8.84 (d, $J_{H-C} = 151.8$ Hz, 1H), 8.67 (d, $J = 7.7$ Hz, 1H), 8.52 (dd, $J_{H-F} = 10.0$, 6.5 Hz, 1H), 8.24 (d, $J_{H-C} = 3.9$ Hz, 1H), 8.22 (d,
$J_{H-C} = 4.1$ Hz, 1H), 7.94 – 7.88 (m, 1H), 7.79 (td, $J = 7.6$, 1.4 Hz, 1H), 7.76 (td, $J = 7.4$, 0.9 Hz, 1H), 7.72 (s, 1H), 7.72 (s, 1H), 7.69 (t, $J = 7.6$ Hz, 1H), 7.28 – 7.20 (m, 8H), 7.16 (d, $J = 7.1$ Hz, 8H), 2.64 – 2.50 (m, 8H), 1.58 (p, $J = 7.9$, 7.5 Hz, 8H), 1.41 – 1.20 (m, 24H), 0.91 – 0.78 (m, 12H). $^{19}$F{$^1$H} NMR (564 MHz, CD$_2$Cl$_2$) $\delta$ -123.98 (d, $J_{F-F} = 19.2$ Hz), -125.11 (d, $J_{F-F} = 19.1$ Hz). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) $\delta$ 188.4, 186.1, 160.7, 158.7, 156.2, 156.1, 156.0, 155.9, 155.8, 153.9, 153.8, 152.8, 148.1, 147.9, 147.4, 146.7, 144.4, 144.2, 144.2, 143.2, 143.1, 140.5, 140.5, 140.2, 140.0, 139.7, 139.4, 139.3, 139.3, 138.9, 138.8, 138.6 (strong), 138.3 (strong), 138.0, 137.8, 137.7, 137.6, 137.4, 137.3, 137.2, 137.1, 137.1, 137.0, 135.6, 135.1, 135.0, 134.9, 129.2, 128.3, 128.3, 125.6, 124.1, 123.9, 123.3, 122.8, 122.2, 119.0, 118.9, 115.3, 115.2, 115.1, 115.0, 114.7, 114.6, 113.1, 112.9, 70.5, 70.1, 63.6, 35.9, 32.1, 31.8, 29.5, 23.0, 14.2. HRMS Calcd for [C$_{92}$H$_{80}$F$_2$N$_4$O$_2$S$_4$ + H]$^+$, m/z = 1465.5272. Found: m/z = 1465.5193 [M+H]$^+$.

Scheme S4. Synthesis of PBDB-TF.

PBDB-TF: PBDB-TF was prepared following a reported procedure.$^6$ $M_n = 18.0$ kg/mol, $D = 2.01$. 

S13
3. UV-vis Absorption Spectroscopy

The ITIC-nF solution and film UV-vis spectra were recorded on a Varian Cary 100 UV-vis spectrophotometer. The ITIC-nF solutions were prepared at 0.0100 mg/mL in chlorobenzene and measured at ambient temperature. The ITIC-nF film optical absorption spectra were recorded from films cast from chlorobenzene (10.0 mg/mL, 2000 rpm) onto glass slides.

Figure S1. Solution UV-vis absorption spectra of the ITIC-nF.

Table S1. Summary of the optical properties of the ITIC-nF and donor polymer.

<table>
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<th>Material</th>
<th>Solution $\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon \times 10^{-5}$ (M$^{-1}$cm$^{-1}$)$^\dagger$</th>
<th>Film $\lambda_{\text{max}}$ (nm)</th>
<th>Onset (nm)$^§$</th>
<th>$E_{\text{g}}^{\text{opt}}$ (eV)$^#$</th>
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<tr>
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<td>806</td>
<td>1.538</td>
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<tr>
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<td>820</td>
<td>1.512</td>
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<td>617</td>
<td>-</td>
<td>621</td>
<td>670</td>
<td>1.851</td>
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</table>

$^\dagger$ Extinction coefficient in chlorobenzene solution (0.0100 mg/mL).  $^§$ Absorption edge of thin film.  $^#$ Optical energy gap estimated from the absorption edge of the thin film.
4. Cyclic Voltammetry (CV)

The electrochemical properties of the ITIC-\(n\)F NFAs were investigated as thin films in deoxygenated anhydrous acetonitrile under \(N_2\) at a scan rate of 100 mV/s using 0.1 M tetrakis(\(n\)-butyl)ammonium hexafluorophosphate \([\text{(n-Bu)}_4\text{N}^+\text{PF}_6^-]\) as the supporting electrolyte. Pt electrodes were used as both the working and counter electrodes, and with Ag/Ag\(^+\) (sat. NaCl) as the pseudoreference electrode. NFAs films were drop-cast onto the Pt working electrode from a 5 mg/mL CHCl\(_3\) solution. A ferrocene/ferrocenium (Fc/Fc\(^+\)) redox couple was used as internal standard and was assigned an absolute energy of \(-4.88\) eV vs vacuum.\(^7\) The HOMO energies of materials were determined according to the equation \(E_{\text{HOMO}} = -(E_{\text{ox onset}} + 4.88)\), where \(E_{\text{ox onset}}\) is the potential at the onset of oxidation relative to the measured Fc/Fc\(^+\) redox couple. The Fc/Fc\(^+\) redox couple was found at 0.447 V relative to the Ag/Ag\(^+\) electrode.

![Cyclic voltammograms of the ITIC-nF NFAs.](image)

**Figure S2.** Cyclic voltammograms of the ITIC-nF NFAs.

**Table S2.** Summary of the electrochemical properties of the ITIC-nF and donor polymer.

<table>
<thead>
<tr>
<th>Material</th>
<th>(E_{\text{ox onset}}) vs. Fc/Fc(^+) (eV)</th>
<th>(E_{\text{HOMO}})(^\dagger) (eV)</th>
<th>(E_{\text{red onset}}) vs. Fc/Fc(^+) (eV)</th>
<th>(E_{\text{LUMO}})(^\ddagger) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITIC-0F(^6)</td>
<td>0.824</td>
<td>-5.70</td>
<td>-0.884</td>
<td>-4.00</td>
</tr>
<tr>
<td>ITIC-2F</td>
<td>0.881</td>
<td>-5.76</td>
<td>-0.807</td>
<td>-4.07</td>
</tr>
<tr>
<td>ITIC-4F</td>
<td>0.864</td>
<td>-5.74</td>
<td>-0.733</td>
<td>-4.15</td>
</tr>
<tr>
<td>ITIC-3F</td>
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<td>-5.73</td>
<td>-0.758</td>
<td>-4.12</td>
</tr>
<tr>
<td>ITIC-6F</td>
<td>0.897</td>
<td>-5.78</td>
<td>-0.720</td>
<td>-4.16</td>
</tr>
<tr>
<td>PBDB-TF(^6)</td>
<td>0.777</td>
<td>-5.66</td>
<td>-</td>
<td>-3.81(^\S)</td>
</tr>
</tbody>
</table>

\(^\dagger\) Calculated according to: \(E_{\text{HOMO}} = -(E_{\text{ox onset}} + 4.88)\). \(^\ddagger\) Calculated according to \(E_{\text{LUMO}} = -(E_{\text{red onset}} + 4.88)\). \(^\S\) Calculated according to: \(E_{\text{LUMO}} = E_g^{\text{opt}} + E_{\text{HOMO}}\).
5. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) measurements were performed on an indium- calibrated Mettler-Toledo DSC822e equipped with a TSO801RO autosampler. The samples (weight range 1.0 – 2.6 mg) were placed in lidded 40 µL Al pans and thermally cycled twice under nitrogen with a heating/cooling rate of 10 °C/min. The reported data correspond to the first cycle and no thermal transitions were observed on second cycle. All data are reported endo up.

![Figure S3](image.png)

**Figure S3.** DSC heating and cooling traces of the ITIC-*n* NFAs.

**Table S3.** Summary of DSC data for the ITIC-*n* NFAs.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{cp}$ (°C)(^a)</th>
<th>$T_c$ (°C)(^b)</th>
<th>$\Delta H$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITIC-2F</td>
<td>207</td>
<td>202</td>
<td>10.4</td>
</tr>
<tr>
<td>ITIC-4F</td>
<td>251(^c)</td>
<td>243(^c)</td>
<td>4.2(^c)</td>
</tr>
<tr>
<td>ITIC-3F</td>
<td>225</td>
<td>213</td>
<td>22.9</td>
</tr>
<tr>
<td>ITIC-6F</td>
<td>249</td>
<td>243</td>
<td>4.4</td>
</tr>
</tbody>
</table>

\(^a\) peak minima (exotherm). \(^b\) the onset temperature of the crystallization exotherm. \(^c\) Melting (endothermic) transition observed.
6. DFT and Semi-Empirical Calculations

6.1. ITIC-nF Single-Crystal Electronic Coupling Calculations

Electronic coupling between all non-equivalent nearest neighbors relative to arbitrarily selected molecules within the ITIC-nF crystal structures were calculated and analyzed according to procedures in our previous report. The transfer integrals were calculated at the ZINDO level of theory as implemented in the ORCA software package and using the projection method implemented in a python package developed in-house. The crystal structures of ITIC-nF were ‘cleaned’ whenever necessary by removing solvent molecules and disordered alkyl chains using the CCDC Mercury software.

Following selection of an arbitrary ITIC-nF molecule in the unit cell as a reference, molecular pairs were defined between the arbitrary molecule and all surrounding molecules with atoms within 10 Å from the reference. Electronic couplings were then calculated for each molecular pair. The molecules surrounding the arbitrary central molecule were then ranked according to the absolute value of the electronic coupling, |J|, between them and the central molecule. Calculated couplings, together with the corresponding intermolecular distances and vector components are reported in Tables S4–S6.

The spatial distribution of electronic couplings was analyzed by summing all the contributions to electronic couplings along a given crystallographic axis i as denoted in Equation 1:

\[ J_i = \sum_{k=1}^{N} \frac{J_{ik}r_{ik}^2}{r_{ik}^2} \]  
(Equation 1)

where \( N \) is the number of nearest neighbors reported in Tables S4–S6, \( J_k \) and \( r_k^2 \) refer to individual neighbors. In order to highlight the directionality with respect to the absolute values of \( J_i \), the results were also normalized by \( J_{tot} \), the sum over all electronic couplings above a 0.1 meV threshold (see Figure S4).

Table S4. Electronic couplings and distance vectors of ITIC-0F.

| |J| (meV) | r (Å) | ra (Å) | rb (Å) | rc (Å) |
|---|---|---|---|---|---|
| 11.42 | 19.419 | 7.570 | -13.889 | 11.264 |
| 3.92 | 23.989 | 15.990 | -13.889 | 11.264 |
| 0.57 | 14.554 | -1.294 | 9.126 | 11.264 |
| 0.57 | 14.554 | 1.294 | -9.126 | -11.264 |

Because the ITIC-4F unit cell contains two non-equivalent molecules, both were used as ‘reference’ to define molecular pairs. The configuration shown in Figure 2b captures the greatest electronic coupling.
Table S5. Electronic couplings and distance vectors of ITIC-4F.

| |J| (meV) | r (Å) | r_a (Å) | r_b (Å) | r_c (Å) |
|---|---|---|---|---|---|
| 17.1 | 7.711 | -7.711 | 0.000 | 0.000 |
| 17.1 | 7.711 | 7.711 | 0.000 | 0.000 |
| 2.8 | 21.557 | 12.731 | -17.396 | 0.000 |
| 2.8 | 21.557 | -12.731 | 17.396 | 0.000 |
| 0.6 | 30.459 | 23.186 | -4.726 | -19.179 |
| 0.6 | 30.459 | -23.186 | 4.726 | 19.179 |

Table S6. Electronic couplings and distance vectors of ITIC-6F.

| |J| (meV) | r (Å) | r_a (Å) | r_b (Å) | r_c (Å) |
|---|---|---|---|---|---|
| 56.8 | 20.073 | -13.279 | 15.053 | 0.000 |
| 56.8 | 20.074 | 13.279 | -15.053 | 0.000 |
| 45.2 | 15.834 | -4.910 | 15.053 | 0.000 |
| 45.2 | 15.834 | 4.910 | -15.053 | 0.000 |
| 0.4 | 8.369 | -8.369 | 0.000 | 0.000 |
| 0.4 | 8.369 | 8.369 | 0.000 | 0.000 |

Figure S4. Directional distribution of electronic coupling in ITIC-nF crystals along the a, b, and c crystallographic axes calculated using Equation 1. Left: values normalized by $J_{tot}$. Right: values (in meV) are not normalized.
6.2. Optimized ITIC-\(n\)F Geometries, Frontier Orbitals, and Internal Reorganization Energies

The ITIC-\(n\)F were optimized at B3LYP/DZP level using the ADF software suite, and the orbitals plotted in Figures S5–S8 were generated from these calculations.\(^{12}\) Reorganization energies were calculated at the same level of theory as previously detailed.\(^{8}\) Excited state absorption spectra were calculated at the ZINDO/S level of theory using the ORCA software suite.\(^{9}\) The \(n\)-hexyl alkyl substituents were replaced with hydrogen atoms.

Figure S5. FMOs of ITIC-2F. (a) LUMO, (b) LUMO+1, (c) HOMO-1, (d) HOMO.

Figure S6. FMOs of ITIC-3F. (a) LUMO, (b) LUMO+1, (c) HOMO-1, (d) HOMO.
**Figure S7.** FMOs of ITIC-4F. (a) LUMO, (b) LUMO+1, (c) HOMO-1, (d) HOMO.

**Figure S8.** FMOs of ITIC-6F. (a) LUMO, (b) LUMO+1, (c) HOMO-1, (d) HOMO.

**Table S7.** Calculated ITIC-$n$F orbital energies, internal reorganization energies ($\lambda_{\text{int}}$), electron affinities (EA) and lowest absorption peaks $\lambda_{\text{max}}$.

<table>
<thead>
<tr>
<th>NFA</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>LUMO+1 (eV)</th>
<th>H-L gap (eV)</th>
<th>EA (eV)</th>
<th>$\lambda_{\text{int}}$ (eV)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITIC-0F</td>
<td>-6.43</td>
<td>-4.25</td>
<td>-3.97</td>
<td>2.18</td>
<td>3.12</td>
<td>0.155</td>
<td>677</td>
</tr>
<tr>
<td>ITIC-2F</td>
<td>-6.41</td>
<td>-4.27</td>
<td>-3.97</td>
<td>2.15</td>
<td>3.11</td>
<td>0.158</td>
<td>671</td>
</tr>
<tr>
<td>ITIC-4F</td>
<td>-6.50</td>
<td>-4.36</td>
<td>-4.09</td>
<td>2.15</td>
<td>3.20</td>
<td>0.158</td>
<td>675</td>
</tr>
<tr>
<td>ITIC-3F</td>
<td>-6.44</td>
<td>-4.33</td>
<td>-4.01</td>
<td>2.11</td>
<td>3.15</td>
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<tr>
<td>ITIC-6F</td>
<td>-6.54</td>
<td>-4.44</td>
<td>-4.18</td>
<td>2.10</td>
<td>3.28</td>
<td>0.147</td>
<td>690</td>
</tr>
</tbody>
</table>
6.3. Fluorination Effects on the End-Group FMOs.

To better understand the subtle effects of ITIC-\(n\)F fluorination on the FMO energies and nodal signatures, we examined a series of fluorinated end-group fragments (Figure S9). Fluorination affects the HOMO and LUMO differently. Specifically, the nodal features of the HOMO depend on the position and number of fluorine atoms, which is consistent with a resonance effect, i.e. fluorine donates electron density from its lone pairs into the \(\pi\)-system. On the other hand, the resonance effect in the LUMO is limited. However, note that fluorination more significantly impacts the LUMO energy than the HOMO energy (Figure S9b), which is also consistent with the ITIC-\(n\)F data in Table S7. 2Fa, 2Fb and 3F all have the same LUMO symmetry, and are equally affected by the resonance effect, but interestingly the LUMOs of 2Fa and 2Fb are degenerate while the LUMO of 3F is slightly lower, due to a higher electron withdrawing effect.

We also observe that fluorination in the 4-position has a larger LUMO-stabilizing effect than does fluorination in the 5- or 6-positions (0F vs 1Fa vs 1Fb vs 1Fc, Figure S9). This observation is in stark contrast to the CV-derived ITIC-\(n\)F LUMO energies (Table S2) and PSC \(V_{OC}\) values (Table S10), where ITIC-3F and ITIC-6F exhibited marginal LUMO energy and \(V_{OC}\) decreases relative to ITIC-2F and ITIC-4F, respectively. This discrepancy between the results of the experimental CV measurements (Figure S2) and \(V_{OC}\) values (Table S10) versus these gas phase computations may be attributable to the varied influences of different interactions/stabilizations present in the solid state. Note that dramatic differences between solid state morphologies of the ITIC-\(n\)F are evident in the single-crystal structures (Figure 2) and spin-coated film GIWAXS data (Figure S24).

Figure S9. (a) FMOs of the non-, mono-, di-, and tri-fluorinated end-groups. Top: LUMO. Bottom: HOMO. (b) HOMO–LUMO gap, LUMO, and HOMO energies of the end-groups optimized at the B3LYP/DZP level.
The FMOs of the whole \textbf{ITIC-\textit{n}F} molecules (Figures S5–S8) are more complicated due to mixing between the features of the IDTT core with those of the end-groups. While we see a monotonic \textbf{ITIC-\textit{n}F} LUMO-lowering effect with increasing fluorination extent (Table S7), the \textbf{ITIC-\textit{n}F} LUMO nodal features are only slightly influenced by the fluorine number and position. Interestingly, the \textbf{ITIC-\textit{n}F} LUMO+1 nodal signatures more closely resemble those of the respective end-group LUMO orbitals.

Overall, we show how both the fluorination position and extent play a role in the tuning of orbital energies for the end-group fragments through the interplay of resonance and electron-withdrawing effects. However, these trends are not always mirrored in the acceptor-donor-acceptor systems or experimental results due to the intricacies of energy level mixing and solid state packing/stabilization interactions.
7. Single-Crystal X-ray Diffraction Analysis

Crystal Growth: ITIC-nF (5 mg) samples were dissolved in CH₂Br₂ (1 mL) in a 2 dram vial. This vial was placed into a 10.8 dram vial containing n-heptane (~5 mL; 99%, EMD Millipore Corporation). The larger vial was then sealed tightly and left undisturbed at room temperature until crystal growth occurred (several weeks). Note that for the ITIC-0F + ITIC-4F cocrystal, crystal growth was achieved by a similar procedure, i.e. by vapor diffusion of n-heptane into a CH₂Br₂ solution containing both ITIC-0F and ITIC-4F (1:1 molar ratio, 5 mg/mL combined concentration).

- Crystal Structure Determination for ITIC-0F:
A suitable crystal of C₉₆H₈₆Br₄N₄O₂S₄ (ITIC-0F) was selected and the crystal was mounted on a MITIGEN holder in Paratone oil on a Kappa Apex 2 diffractometer. The crystal was kept at 100.02 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the XL refinement package using Least Squares minimization.

Crystal Data: for C₉₆H₈₆Br₄N₄O₂S₄ (M=1775.56): triclinic, space group P-1 (no. 2), a = 8.420(6) Å, b = 23.019(7) Å, c = 23.126(17) Å, α = 101.780(10)°, β = 95.319(10)°, γ = 91.105(14)°, V = 4366(5) Å³, Z = 2, T = 100.02 K, μ(MoKα) = 1.990 mm⁻¹, Dcalc = 1.351 g/mm³, 50025 reflections measured (1.808 ≤ 2θ ≤ 52.88), 17919 unique (Rint = 0.0406, Rsigma = 0.0563) which were used in all calculations. The final R1 was 0.0960 (I > 2σ(I)) and wR2 was 0.3063 (all data).

Refinement Details: Distance restraints were imposed on the disordered carbon chains. The enhanced rigid-bond restraint (SHELX keyword RIGU) was applied globally.¹⁶

Solvent Treatment Details: The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 434.4 Å³ [10.0%] Total electron count / cell = 113.3

- Crystal Structure Determination for ITIC-4F:
A suitable crystal of C₁₈₈H₁₆₀F₈N₈O₄S₈ (ITIC-4F) was selected and the crystal was mounted on a MITIGEN holder in Paratone oil on a Kappa Apex 2 diffractometer. The crystal was kept at 99.98 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the XL refinement package using Least Squares minimization.

Crystal Data for C₁₈₈H₁₆₀F₈N₈O₄S₈ (M=3003.71): triclinic, space group P-1 (no. 2), a = 15.4222(8) Å, b = 17.6025(11) Å, c = 21.1852(12) Å, α = 73.995(4)°, β = 68.809(4)°, γ = 81.206(4)°, V = 5145.3(5) Å³, Z = 1, T = 99.98 K, μ(CuKα) = 1.231 mm⁻¹, Dcalc = 0.969 g/mm³,
91137 reflections measured (4.608 \leq 2\Theta \leq 128.394), 16789 unique (R_{int} = 0.1180, R_{sigma} = 0.0891) which were used in all calculations. The final R_1 was 0.1504 (I > 2\sigma(I)) and wR_2 was 0.4355 (all data).

**Refinement Details.** Rigid bond restraints were imposed on the displacement parameters as well as restraints on similar amplitudes separated by less than 1.7 Å globally. Distance restraints were imposed on the carbon chains. Disordered C11 and C11a C21 were restrained esd that their U_{ij} components approximate to isotropic.

**Solvent Treatment Details.** The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 1763.9 Å^3 [34.6%] Total electron count / cell = 417.6

- **Crystal Structure Determination for ITIC-6F:**

A suitable crystal of C_{94}H_{76}F_{6}N_{4}O_{2}S_{4} (ITIC-6F) was selected and the crystal was mounted on a MITIGEN holder in Paratone oil on a Kappa Apex 2 diffractometer. The crystal was kept at 100.0 K during data collection. Using Olex2,^{13} the structure was solved with the ShelXT^{14} structure solution program using Intrinsic Phasing and refined with the ShelXL^{17} refinement package using Least Squares minimization.

**Crystal Data** for C_{94}H_{76}F_{6}N_{4}O_{2}S_{4} (M=1535.82): triclinic, space group P-1 (no. 2), a = 8.3692(4) Å, b = 15.4456(7) Å, c = 18.9453(10) Å, \alpha = 68.171(3)^{0}, \beta = 88.703(4)^{0}, \gamma = 77.059(3)^{0}, V = 2210.69(19) Å^3, Z = 1, T = 100.0 K, \mu(CuK\alpha) = 1.478 mm^{-1}, D_{calc} = 1.154 g/mm^3, 13387 reflections measured (5.036 \leq 2\Theta \leq 130.412), 7259 unique (R_{int} = 0.0394, R_{sigma} = 0.0626) which were used in all calculations. The final R_1 was 0.1234 (I > 2\sigma(I)) and wR_2 was 0.3243 (all data).

**Refinement Details:** No special refinement necessary.

**Solvent Treatment Details:** The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 390.8 Å^3 [17.7%] Total electron count / cell = 209.5

- **Crystal Structure Determination for ITIC-2F:**

Single crystals of C_{94}H_{80}F_{2}N_{4}O_{2}S_{4} (ITIC-2F) were supplied. A suitable crystal was selected and the crystal was mounted on a MITIGEN holder with Paratone oil on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 99.99 K during data collection. Using Olex2,^{13} the structure was solved with the ShelXT^{14} structure solution program using Intrinsic Phasing and refined with the XL^{15} refinement package using Least Squares minimization.
Crystal Data for C$_{94}$H$_{80}$F$_{2}$N$_{4}$O$_{2}$S$_{4}$ ($M=1463.86$): triclinic, space group P-1 (no. 2), $a = 15.5206(9)$ Å, $b = 17.8326(16)$ Å, $c = 20.9600(19)$ Å, $\alpha = 72.141(8)^\circ$, $\beta = 68.454(6)^\circ$, $\gamma = 80.226(7)^\circ$, $V = 5125.1(8)$ Å$^3$, $Z = 2$, $T = 99.99$ K, $\mu$(CuKα) = 1.197 mm$^{-1}$, $D_{calc} = 0.949$ g/mm$^3$, 26604 reflections measured ($4.702 \leq 2\Theta \leq 123.064$), 15232 unique ($R_{int} = 0.1431$, $R_{sigma} = 0.2274$) which were used in all calculations. The final $R_1$ was 0.2316 ($I > 2\sigma(I)$) and $wR_2$ was 0.5329 (all data).

Refinement Details. The enhanced rigid-bond restraint (SHELX keyword RIGU) was applied globally. Uij components were restrained approximate to isotropic (SHELX ISOR)) globally. Distance restraints were imposed on the carbon chains.

Solvent Treatment Details. The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 1758.6 Å$^3$ [34.3%] Total electron count / cell = 525.6

Redistribution Analysis. Single-crystals of ITIC-2F were subjected to $^{19}$F{¹H} NMR spectroscopy analysis to determine the extent of redistribution occurring during crystal growth. No redistributed products were observed.

Disorder Note. The ITIC-2F molecules are found to be disordered over the inversion center. Both nonfluorinated and difluorinated end-groups are disordered between the same positions. Also, the fluorine displacement parameters indicate that they are only half occupied.

Crystal Structure Determination for ITIC-0F:ITIC-4F Cocrystal:

A suitable crystal of ITIC-0F:ITIC-4F was selected and the crystal was mounted on a MITIGEN holder in Paratone oil on a Bruker Kappa APEX CCD area detector diffractometer. The crystal was kept at 100.0 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the XL refinement package using Least Squares minimization.

Crystal Data for C$_{189}$H$_{162}$Br$_2$F$_4$N$_8$O$_4$S$_8$ ($M=3101.56$): triclinic, space group P-1 (no. 2), $a = 15.4670(5)$ Å, $b = 17.5307(7)$ Å, $c = 20.7381(8)$ Å, $\alpha = 82.827(3)^\circ$, $\beta = 68.565(2)^\circ$, $\gamma = 80.934(2)^\circ$, $V = 5154.9(3)$ Å$^3$, $Z = 1$, $T = 100.0$ K, $\mu$(CuKα) = 1.650 mm$^{-1}$, $D_{calc} = 0.999$ g/mm$^3$, 29823 reflections measured ($4.59 \leq 2\Theta \leq 124.758$), 14834 unique ($R_{int} = 0.0478$, $R_{sigma} = 0.0695$) which were used in all calculations. The final $R_1$ was 0.1532 ($I > 2\sigma(I)$) and $wR_2$ was 0.4418 (all data).

Refinement Details. Distance restraints were imposed on the carbon chains. Restraints on similar amplitudes (esd 0.05) separated by less than 1.7 Å was refined globally.

Solvent Treatment Details. The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement. As the exact
solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 1695.1 Å³ [32.9%] Total electron count / cell = 680.9

**Composition/Disorder Note.** While the exact ratio of ITIC-0F:ITIC-4F within the cocrystal is not known, the fluorine displacement parameters indicate that they are only partially occupied and that some nonfluorinated end-groups of ITIC-0F are present. The molecules within the cocrystal are found to be disordered over the inversion center. Both nonfluorinated and difluorinated groups disorder between the same positions. It is reasonable to assume that because redistribution does not occur during the growth of the ITIC-2F single-crystal, it also likely does not occur during the growth of this cocrystal.
<table>
<thead>
<tr>
<th></th>
<th>ITIC-0F</th>
<th>ITIC-4F</th>
<th>ITIC-6F</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCDC Deposition Number</td>
<td>1885952</td>
<td>1885953</td>
<td>1885954</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₉₆H₈₆Br₄N₄O₂S₄</td>
<td>C₁₈₈H₁₆₀F₈N₈O₄S₈</td>
<td>C₉₄H₇₆F₆N₄O₂S₄</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1775.56</td>
<td>3003.71</td>
<td>1535.82</td>
</tr>
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<td>Temperature /K</td>
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<td>99.98</td>
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<tr>
<td>a / Å, b / Å, c / Å</td>
<td>8.420(6), 23.019(17), 23.126(17)</td>
<td>15.4222(8), 17.6025(11), 21.1852(12)</td>
<td>8.3692(4), 15.4456(7), 18.9453(10)</td>
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<td>α°, β°, γ°</td>
<td>101.780(10), 95.319(10), 91.105(14)</td>
<td>73.995(4), 68.809(4), 81.206(4)</td>
<td>68.171(3), 88.703(4), 77.059(3)</td>
</tr>
<tr>
<td>Volume /Å³</td>
<td>4366(5)</td>
<td>5145.3(5)</td>
<td>2210.69(19)</td>
</tr>
<tr>
<td>Z</td>
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<td>1</td>
<td>1</td>
</tr>
<tr>
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<td>1.351</td>
<td>0.969</td>
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<td>μ / mm&lt;sup&gt;-1&lt;/sup&gt;</td>
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<td>802</td>
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<td>Crystal size /mm&lt;sup&gt;3&lt;/sup&gt;</td>
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<td>0.475 × 0.065 × 0.055</td>
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<td>5.036 to 130.412°</td>
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<td>Index ranges</td>
<td>-10 ≤ h ≤ 10, -28 ≤ k ≤ 28, -28 ≤ l ≤ 28</td>
<td>-16 ≤ h ≤ 17, -20 ≤ k ≤ 20, -24 ≤ l ≤ 24</td>
<td>-5 ≤ h ≤ 9, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>50025</td>
<td>91137</td>
<td>13387</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>17919[R(int) = 0.0406]</td>
<td>16789[R(int) = 0.1180]</td>
<td>7259[R(int) = 0.0394]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>17919/1645/1103</td>
<td>16789/1886/1136</td>
<td>7259/0/527</td>
</tr>
<tr>
<td>Goodness-of-fit on F&lt;sup&gt;2&lt;/sup&gt;</td>
<td>1.041</td>
<td>1.610</td>
<td>1.062</td>
</tr>
<tr>
<td>Final R indexes [I&gt;2σ (I)]</td>
<td>R&lt;sub&gt;1&lt;/sub&gt; = 0.0960, wR&lt;sub&gt;2&lt;/sub&gt; = 0.2792</td>
<td>R&lt;sub&gt;1&lt;/sub&gt; = 0.1504, wR&lt;sub&gt;2&lt;/sub&gt; = 0.4104</td>
<td>R&lt;sub&gt;1&lt;/sub&gt; = 0.1234, wR&lt;sub&gt;2&lt;/sub&gt; = 0.3163</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R&lt;sub&gt;1&lt;/sub&gt; = 0.1266, wR&lt;sub&gt;2&lt;/sub&gt; = 0.3063</td>
<td>R&lt;sub&gt;1&lt;/sub&gt; = 0.1853, wR&lt;sub&gt;2&lt;/sub&gt; = 0.4355</td>
<td>R&lt;sub&gt;1&lt;/sub&gt; = 0.1367, wR&lt;sub&gt;2&lt;/sub&gt; = 0.3243</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>2.243/-3.642</td>
<td>1.837/-0.778</td>
<td>1.338/-0.854</td>
</tr>
</tbody>
</table>
**Table S9.** Crystallographic data and structural refinement for ITIC-2F, and ITIC-0F:ITIC-4F cocrystal.

<table>
<thead>
<tr>
<th></th>
<th>ITIC-2F</th>
<th>ITIC-0F:ITIC-4F</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CCDC Deposition Number</strong></td>
<td>1885955</td>
<td>1885956</td>
</tr>
<tr>
<td><strong>Empirical formula</strong></td>
<td>$\text{C}<em>{94}\text{H}</em>{80}\text{F}<em>{2}\text{N}</em>{4}\text{O}<em>{2}\text{S}</em>{4}$</td>
<td>$\text{C}<em>{189}\text{H}</em>{362}\text{Br}<em>{2}\text{F}</em>{4}\text{N}<em>{8}\text{O}</em>{4}\text{S}_{8}$</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>1463.86</td>
<td>3101.56</td>
</tr>
<tr>
<td><strong>Temperature / K</strong></td>
<td>99.99</td>
<td>100.0</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td><strong>a / Å, b / Å, c / Å</strong></td>
<td>15.5206(9), 17.8326(16), 20.9600(19)</td>
<td>15.4670(5), 17.5307(7), 20.7381(8)</td>
</tr>
<tr>
<td><strong>α/°, β/°, γ/°</strong></td>
<td>72.141(8), 68.454(6), 80.226(7)</td>
<td>82.827(3), 68.565(2), 80.934(2)</td>
</tr>
<tr>
<td><strong>Volume / Å³</strong></td>
<td>5125.1(8)</td>
<td>5154.9(3)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td><strong>$\rho_{\text{calc}}$ / mg mm$^{-3}$</strong></td>
<td>0.949</td>
<td>0.999</td>
</tr>
<tr>
<td><strong>$\mu$ / mm$^{-1}$</strong></td>
<td>1.197</td>
<td>1.650</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>1540</td>
<td>1618</td>
</tr>
<tr>
<td><strong>Crystal size / mm$^3$</strong></td>
<td>$? \times ? \times ?$</td>
<td>$0.568 \times 0.072 \times 0.064$</td>
</tr>
<tr>
<td><strong>2Θ range for data collection</strong></td>
<td>4.702 to 123.064°</td>
<td>4.59 to 124.758°</td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>-17 ≤ h ≤ 15, -20 ≤ k ≤ 12, -23 ≤ l ≤ 17</td>
<td>-17 ≤ h ≤ 15, -20 ≤ k ≤ 20, -23 ≤ l ≤ 19</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>26604</td>
<td>29823</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>15232[R(int) = 0.1431]</td>
<td>14834[R(int) = 0.0478]</td>
</tr>
<tr>
<td><strong>Data/restraints/parameters</strong></td>
<td>15232/1873/973</td>
<td>14834/781/1002</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F$^2$</strong></td>
<td>1.614</td>
<td>1.773</td>
</tr>
<tr>
<td><strong>Final R indexes [I&gt;2σ (I)]</strong></td>
<td>$R_1 = 0.2316, wR_2 = 0.5059$</td>
<td>$R_1 = 0.1532, wR_2 = 0.4224$</td>
</tr>
<tr>
<td><strong>Final R indexes [all data]</strong></td>
<td>$R_1 = 0.2814, wR_2 = 0.5329$</td>
<td>$R_1 = 0.1754, wR_2 = 0.4418$</td>
</tr>
<tr>
<td><strong>Largest diff. peak/hole / e Å$^{-3}$</strong></td>
<td>0.940/-0.885</td>
<td>1.453/-0.741</td>
</tr>
</tbody>
</table>


Figure S10. Single crystal X-ray structure for **ITIC-0F** from two perspectives. Thermal ellipsoids at 50% probability. Hydrogen atoms omitted for ease of viewing.

Figure S11. Single crystal X-ray structure for **ITIC-4F** from two perspectives. Thermal ellipsoids at 50% probability. Hydrogen atoms omitted for ease of viewing.

Figure S12. Single crystal X-ray structure for **ITIC-6F** from two perspectives. Thermal ellipsoids at 50% probability. Hydrogen atoms omitted for ease of viewing.
**Figure S13.** Single crystal X-ray structure for ITIC-2F from two perspectives. Thermal ellipsoids at 50% probability. Hydrogen atoms omitted for ease of viewing. Note that the fluorine atoms (green) are only 50% occupied; the other 50% are occupied by hydrogens.

**Figure S14.** Crystal X-ray structure for ITIC-0F:ITIC-4F cocrystal from two perspectives. Thermal ellipsoids at 50% probability. Hydrogen atoms omitted for ease of viewing. Note that the fluorine atoms (green) are only partially occupied; some end-groups occupying the same position are nonfluorinated.
8. NMR Spectroscopy

**Compound 1**

- $^1$H NMR, 400 MHz
- (CD$_3$)$_2$SO

**Compound 1**

- $^{19}$F NMR, 376 MHz
- (CD$_3$)$_2$SO
Compound 4
\(^1\)H NMR, 500 MHz
CDCl\(_3\)

Compound 4
\(^{19}\)F NMR, 470 MHz
CDCl\(_3\)
Compound 4
$^{13}$C NMR, 126 MHz
CDCl$_3$

Compound 5
$^1$H NMR, 400 MHz
CD$_2$Cl$_2$
Compound 6
$^1$H NMR, 400 MHz
CDCl$_3$

Compound 7
$^1$H NMR, 400 MHz
CDCl$_3$
Compound 7
$^{19}$F NMR, 376 MHz
CDCl$_3$

Compound 8
$^1$H NMR, 500 MHz
CD$_2$Cl$_2$
Compound 8
$^{13}$C NMR, 126 MHz
CD$_2$Cl$_2$

ITIC-OF
$^1$H NMR, 500 MHz
CD$_2$Cl$_2$
ITIC-4F
$^1$H NMR, 500 MHz
CD$_2$Cl$_2$
ITIC-6F
$^1$H NMR, 500 MHz
CD$_2$Cl$_2$

$^1$H{$^{19}$F} NMR, 500 MHz
CD$_2$Cl$_2$

$^1$H NMR, 500 MHz
CD$_2$Cl$_2$
ITIC-6F
$^{13}$C NMR, 126 MHz
CD$_2$Cl$_2$
ITIC-3F
\(^{19}\text{F NMR, 470 MHz}\)
\(\text{CD}_2\text{Cl}_2\)

\[\begin{array}{c}
\text{20.2} & \text{-120.4} & \text{-120.8} & \text{-136.4} & \text{-136.6} & \text{-136.8} & \text{-149.1} & \text{-149.3} & \text{-149.5} \\
\end{array}\]

\[\begin{array}{c}
\text{20} & \text{10} & \text{0} & \text{-10} & \text{-20} & \text{-30} & \text{-40} & \text{-50} & \text{-60} & \text{-70} & \text{-80} & \text{-90} & \text{-100} & \text{-110} & \text{-120} & \text{-130} & \text{-140} & \text{-150} & \text{-160} & \text{-170} & \text{-180} & \text{-190} \\
\end{array}\]

\text{ITIC-3F}
\(^{19}\text{F\text{'}(H)} \text{NMR, 470 MHz}\)
\(\text{CD}_2\text{Cl}_2\)

\[\begin{array}{c}
\text{-120.25} & \text{-120.35} & \text{-120.45} & \text{-120.55} & \text{-136.40} & \text{-136.50} & \text{-136.60} & \text{-149.15} & \text{-149.25} & \text{-149.35} & \text{-149!} \\
\end{array}\]
Compound 10
$^1$H NMR, 500 MHz
CD$_2$Cl$_2$

Compound 10
$^{13}$C NMR, 126 MHz
CD$_2$Cl$_2$
$^{13}$CHO-IDTT($^{13}$C)-0F

$^1$H NMR, 600 MHz
CD$_2$Cl$_2$

$^{13}$CHO-IDTT($^{13}$C)-0F

$^{13}$C NMR, 126 MHz
CD$_2$Cl$_2$
ITIC(\(^{13}\)C)-4F
\(^1\)H NMR, 600 MHz
CD\(_2\)Cl\(_2\)

13\(^{13}\)F(\(^1\)H) NMR, 564 MHz
CD\(_2\)Cl\(_2\)
ITIC\textsuperscript{\textsuperscript{13}C}-2F
\textsuperscript{1}H NMR, 600 MHz
CD\textsubscript{2}Cl\textsubscript{2}

ITIC\textsuperscript{\textsuperscript{13}C}-2F
\textsuperscript{19}F\textsuperscript{\textsuperscript{1}H} NMR, 564 MHz
CD\textsubscript{2}Cl\textsubscript{2}
9. Solar Cell Device Fabrication and Characterization

An “inverted” device architecture, indium tin oxide (ITO)/ZnO/PBDB-TF:ITIC-nF/MoOx/Ag, was used. Pre-patterned ITO-coated glass wafers (Thin Film Devices, Inc.) with a thickness of ~280 nm and sheet resistance of ~20 Ω/sq were used as substrates. ITO electrodes were cleaned by sequential sonication in aqueous detergent solution, deionized water, methanol, acetone, and isopropanol. Finally, the ITO electrodes were cleaned with a UV/ozone treatment (Jelight Co.) for 15 min. The cathode interfacial layer, ZnO, was deposited from a precursor solution of 0.5 M zinc acetate dihydrate and 0.5 M 2-aminoethanol in 2-methoxyethanol, which was spun cast at 7000 rpm for 30 s and annealed at 170 °C for 10 min in air. Active layer solutions were prepared in 2 mL screw top amber glass vials in an argon-filled glovebox (< 2 ppm O2 and H2O) by following one of two methods (A or B):

**Method A (“Scrambled”):** PBDB-TF and ITIC-nF (1:1 mass ratio) were dissolved in a PhCl:1,8-diiodooctane (99.5:0.5 v/v) solvent mixture (10.0 mg mL⁻¹ PBDB-TF concentration) and stirred for 16 h at 50 °C in an argon-filled glovebox. Active layer solution was then cooled to ~25 °C over 10 min. and then active layers were spin coated inside glovebox (2500 rpm, 60 s).

**Method B (“Unscrambled”):** PBDB-TF was dissolved in a PhCl:1,8-diiodooctane (99.5:0.5 v/v) solvent mixture (10.0 mg mL⁻¹ PBDB-TF concentration) and stirred for 16 h at 50 °C in an argon-filled glovebox. The PBDB-TF solution was cooled to ~25 °C over 10 min. and then transferred to a vial containing ITIC-nF to achieve a 10.0 mg mL⁻¹ ITIC-nF concentration. The PBDB-TF:ITIC-nF mixtures were stirred at 25 °C for 10 min. and then active layers were spin coated inside glovebox (2500 rpm, 60 s).

**Note:** For ternary mixtures, a 1:1 molar ratio of the two ITIC-nF NFAs was used, and the PBDB-TF:(ITIC-n1F+ITIC-n2F) mass ratio was 1:1 in active layer solutions.

For all devices, the active layer thicknesses are ~100–110 nm. Thin layers of MoOx (9 nm) and Ag (100 nm) were then vapor deposited through a shadow mask with dimensions of 2 mm × 3 mm (device area = 6 mm²) at ~10⁻⁶ Torr.

The photovoltaic characteristics of devices were tested in air at ambient temperature. The current density-voltage (J–V) curves were obtained by a Keithley 2400 source-measure unit using four-point contact measurements. The photocurrent was measured under simulated AM1.5G irradiation (100 mW cm⁻²) using Xe arc lamp of a Spectra-Nova 300W Class-A solar simulator. The light intensity was calibrated using an NREL-certified monocrystalline Si photodiode coupled to a KG3 filter to bring the spectral mismatch to unity. External quantum efficiency (EQE) was measured using Newport QE-PV-SI setup. Incident light from a Xe lamp (300 W) passing through a monochromator (Newport, Cornerstone 260) was focused on the active area of the cell. The output current was measured using a current pre-amplifier (Newport, 70710QE) and a lock-in amplifier (Newport, 70105 Dual channel Merlin). A calibrated silicon diode (Newport 70356) was used as a reference.
### Table S10. Photovoltaic parameters of PBDB-TF:ITIC-nF solar cells.

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>Condition</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)*</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Number of devices (#)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITIC-0F</td>
<td>-</td>
<td>1.000 ± 0.009 (1.004)</td>
<td>14.8 ± 0.4 (15.1)</td>
<td>14.7</td>
<td>56.5 ± 0.9 (57.6)</td>
<td>8.33 ± 0.18 (8.72)</td>
<td>10</td>
</tr>
<tr>
<td>ITIC-2F</td>
<td>-</td>
<td>0.915 ± 0.004 (0.917)</td>
<td>16.7 ± 0.3 (17.3)</td>
<td>16.7</td>
<td>65.6 ± 0.3 (65.7)</td>
<td>10.03 ± 0.17 (10.38)</td>
<td>11</td>
</tr>
<tr>
<td>SCR</td>
<td>-</td>
<td>0.912 ± 0.004 (0.913)</td>
<td>16.3 ± 0.7 (16.9)</td>
<td>16.6</td>
<td>64.8 ± 0.6 (65.5)</td>
<td>9.67 ± 0.44 (10.07)</td>
<td>10</td>
</tr>
<tr>
<td>ITIC-4F</td>
<td>-</td>
<td>0.831 ± 0.006 (0.829)</td>
<td>17.6 ± 0.6 (18.3)</td>
<td>18.1</td>
<td>67.7 ± 0.6 (68.4)</td>
<td>9.91 ± 0.39 (10.39)</td>
<td>16</td>
</tr>
<tr>
<td>ITIC-3F</td>
<td>annealed</td>
<td>0.896 ± 0.005 (0.892)</td>
<td>17.8 ± 0.8 (19.4)</td>
<td>17.2</td>
<td>66.0 ± 0.7 (66.1)</td>
<td>10.55 ± 0.48 (11.44)</td>
<td>12</td>
</tr>
<tr>
<td>SCR</td>
<td>annealed</td>
<td>0.840 ± 0.008 (0.845)</td>
<td>16.7 ± 0.7 (17.6)</td>
<td>16.5</td>
<td>55.0 ± 1.9 (56.3)</td>
<td>7.74 ± 0.50 (8.36)</td>
<td>14</td>
</tr>
<tr>
<td>ITIC-6F</td>
<td>annealed</td>
<td>0.890 ± 0.004 (0.887)</td>
<td>17.9 ± 0.3 (18.4)</td>
<td>16.9</td>
<td>64.1 ± 0.6 (64.5)</td>
<td>10.21 ± 0.22 (10.54)</td>
<td>11</td>
</tr>
<tr>
<td>ITIC-0F:</td>
<td>annealed</td>
<td>0.809 ± 0.006 (0.818)</td>
<td>21.2 ± 0.5 (21.6)</td>
<td>18.7</td>
<td>66.7 ± 1.0 (67.4)</td>
<td>11.41 ± 0.47 (11.89)</td>
<td>12</td>
</tr>
<tr>
<td>ITIC-4F</td>
<td>annealed</td>
<td>0.677 ± 0.004 (0.679)</td>
<td>16.3 ± 0.2 (16.7)</td>
<td>15.6</td>
<td>47.6 ± 1.2 (49.3)</td>
<td>5.25 ± 0.22 (5.57)</td>
<td>8</td>
</tr>
<tr>
<td>SCR</td>
<td>annealed</td>
<td>0.701 ± 0.005 (0.701)</td>
<td>17.0 ± 0.9 (17.7)</td>
<td>16.8</td>
<td>65.2 ± 0.3 (65.8)</td>
<td>9.61 ± 0.60 (10.64)</td>
<td>15</td>
</tr>
<tr>
<td>ITIC-0F:</td>
<td>annealed</td>
<td>0.913 ± 0.005 (0.911)</td>
<td>17.0 ± 0.8 (18.6)</td>
<td>16.7</td>
<td>65.5 ± 0.4 (65.1)</td>
<td>10.19 ± 0.48 (11.01)</td>
<td>13</td>
</tr>
<tr>
<td>ITIC-6F</td>
<td>annealed</td>
<td>0.888 ± 0.005 (0.887)</td>
<td>15.9 ± 0.8 (17.0)</td>
<td>16.2</td>
<td>62.6 ± 0.7 (63.1)</td>
<td>8.84 ± 0.45 (9.51)</td>
<td>12</td>
</tr>
</tbody>
</table>

Photovoltaic parameters are reported as averages ± one standard deviation. Values in parentheses are for the champion cells. * Current density calculated from integration of external quantum efficiency (EQE) spectra of champion device. b Blend prepared following unscrambled conditions and film was annealed at 210 °C for 5 min inside of glovebox before evaporation of MoO$_x$ and Ag. c Thermal annealing performed for 5 min at 240 °C inside of glovebox before evaporation of MoO$_x$ and Ag.
Figure 15. Histograms of power conversion efficiency (PCE) data for PBDB-TF:ITIC-nF solar cell devices.
**10. End-Group Scrambling Analysis in Photovoltaic Blend Solutions.**

Following spin coating of photovoltaic films, the remaining blend solution was removed from the glovebox and then solvent was removed under reduced pressure. The residue was next dissolved in CD$_2$Cl$_2$ at ~ 2 mg mL$^{-1}$ NFA concentration and analyzed by $^{19}$F{$^1$H} NMR spectroscopy as well as HRMS. Scrambling percentage was determined by integration of the $^{19}$F{$^1$H} NMR spectra. We calculate the percentage of scrambled products within the photovoltaic blend solutions from the ratio of the $^{19}$F peak integral of the scrambled byproduct molecule relative to the $^{19}$F peak integral of the original molecule added to the active layer solution as shown in Equation 2. Only $^{19}$F{$^1$H} NMR spectroscopy was employed due to poor resolution/overlap between the different ITIC-$n$F peaks in the $^1$H NMR spectra (Figure S18).

$$\text{Scrambling \%} = \frac{\text{byproduct NFA Fluorine signal}}{\text{unscrambled NFA Fluorine signal}} \times 100\%$$  \hspace{1cm} \text{(Equation 2)}

Table S11. Summary of $^{19}$F{$^1$H} NMR scrambling data for photovoltaic blend solutions.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Condition</th>
<th>Scrambled NFA : Unscrambled NFA</th>
<th>Scrambling %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITIC-2F</td>
<td>unscrambled</td>
<td>3.11 : 97.05</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>scrambled</td>
<td>37.33 : 62.67</td>
<td>59.6</td>
</tr>
<tr>
<td>ITIC-0F:</td>
<td>unscrambled</td>
<td>1.66 : 98.75</td>
<td>1.7</td>
</tr>
<tr>
<td>ITIC-4F</td>
<td>scrambled</td>
<td>25.31 : 74.69</td>
<td>33.9</td>
</tr>
<tr>
<td>ITIC-3F</td>
<td>unscrambled</td>
<td>n.d.</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>scrambled</td>
<td>4.58 : 95.42</td>
<td>4.8</td>
</tr>
<tr>
<td>ITIC-0F:</td>
<td>unscrambled</td>
<td>n.d.</td>
<td>&lt;1</td>
</tr>
<tr>
<td>ITIC-6F</td>
<td>scrambled</td>
<td>4.12 : 95.88</td>
<td>4.3</td>
</tr>
</tbody>
</table>

n.d. = not determined due to weak scrambled NFA signal.
**Figure S16.** Comparison of the $^{19}$F-$^1$H NMR spectra for the purified ITIC-2F and ITIC-4F versus the scrambled and unscrambled photovoltaic blend solution spectra. Scrambling occurs even under light-free conditions, ruling out a photocatalyzed reaction mechanism.

**Figure S17.** Comparison of the $^{19}$F-$^1$H NMR spectra for the purified ITIC-3F and ITIC-6F versus the scrambled photovoltaic blend solution spectra.
Figure S18. Comparison of the $^1$H NMR spectra of purified ITIC-0F, ITIC-2F, and ITIC-4F versus the scrambled photovoltaic blend solution spectra. (top) full (bottom) aromatic region. Note that due to peak overlap, the ITIC-2F spectrum resembles a superposition of the ITIC-0F and ITIC-4F spectra. Consequently, scrambling analysis by $^1$H NMR is uninformative. Additionally, no peaks attributable to aldehyde or cyclobutane species are evident.
ITIC-2F PV blend solution
"unscrambled" conditions

$^{19}$F($^1$H) NMR, 564 MHz
CD$_2$Cl$_2$

ITIC-2F PV blend solution
"scrambled" conditions

$^{19}$F($^1$H) NMR, 470 MHz
CD$_2$Cl$_2$
ITIC-0F:ITIC-4F PV blend solution
"unsymmetrized scrambling" conditions

\(^{19}\text{F}(^1\text{H})\) NMR, 564 MHz
\(\text{CD}_2\text{Cl}_2\)

\[\begin{align*}
-123.5 & -123.7 & -123.9 & -124.1 & -124.3 & -124.5 & -124.7 & -124.9 & -125.1 & -125.3 & -125.5 \\
98.65 & 98.66 & 124.65 & 124.66 & 124.67 & 124.68 & 124.69 & 124.7 & 124.71 & 124.72 & 124.73
\end{align*}\]

---

ITIC-0F:ITIC-4F PV blend solution
"scrambled" conditions

\(^{19}\text{F}(^1\text{H})\) NMR, 470 MHz
\(\text{CD}_2\text{Cl}_2\)

\[\begin{align*}
-125.5 & -125.7 & -125.9 & -126.1 & -126.3 & -126.5 \\
122.68 & 122.69 & 122.7 & 122.71 & 122.72 & 122.73
\end{align*}\]
ITIC-3F PV blend solution
"unsccrambled conditions"
$^{19}$F($^1$H) NMR, 564 MHz
CD$_2$Cl$_2$

ITIC-3F PV blend solution
"scrambled conditions"
$^{19}$F($^1$H) NMR, 470 MHz
CD$_2$Cl$_2$
ITIC-0F:ITIC-6F PV blend solution
"unscrambled conditions"
\(^{19}\text{F}(^{1}\text{H})\text{ NMR, 564 MHz}
\text{CD}_2\text{Cl}_2

ITIC-0F:ITIC-6F PV blend solution
"scrambled conditions"
\(^{19}\text{F}(^{1}\text{H})\text{ NMR, 470 MHz}
\text{CD}_2\text{Cl}_2
Figure S19. HRMS analysis of scrambled binary and ternary photovoltaic blend solutions.
Figure S20. Solvent effects on ITIC-\(n\)F scrambling. ITIC-\(n\)F were dissolved in anhydrous solvent (10 mg/mL) for 16 h at 50 °C and then cooled, solvent was removed under reduced pressure, and then residue was analyzed by \(^{19}\text{F}\{^{1}\text{H}\}\) NMR spectroscopy. Scrambling is found to be more extensive in higher dielectric constant solvent such as 1,2-dichlorobenzene (DCB) and less extensive in lower dielectric constant solvent such as PhMe. The dielectric constants of each solvent are: PhMe (2.4), PhCl (5.6), DCB (9.9).
End-Group Exchange Mechanistic Experiments

Scheme S5. End-group exchange model experiments.

**Reaction A**: PBDB-TF (3.59 mg), ITIC-4F (1.96 mg, 1.3 μmol), and \(^{13}\text{CHO-IDTT}^{(13C)}-\text{0F}\) (1.63 mg, 1.3 μmol) were dissolved in a PhCl:1,8-diiodooctane (99.5:0.5 v/v) solvent mixture (359 μL).

**Reaction B**: PBDB-TF (4.07 mg), ITIC-0F (2.15 mg, 1.5 μmol), and \(^{13}\text{CHO-IDTT}^{(13C)}-\text{2F}\) (1.94 mg, 1.5 μmol) were dissolved in a PhCl:1,8-diiodooctane (99.5:0.5 v/v) solvent mixture (407 μL).

**Reaction C**: PBDB-TF (4.53 mg), ITIC-0F (2.38 mg, 1.67 μmol), and \(^{13}\text{CHO-IDTT}^{(13C)}-\text{2F}\) (2.15 mg, 1.67 μmol) were dissolved in a PhCl:1,8-diiodooctane (99.5:0.5 v/v) solvent mixture (453 μL), removed from glovebox and then H₂O (4.53 μL) was added via syringe. The reaction was then stirred for 24 h at 50 °C.
**Reaction D:** PBDB-TF (1.99 mg), ITIC-6F (1.13 mg, 0.74 μmol), and $^{13}$CHO-IDTT($^{13}$C)-0F (0.94 mg, 0.75 μmol) were dissolved in a PhCl:1,8-diiodooctane (99.5:0.5 v/v) solvent mixture (199 μL).

**Reaction E:** PBDB-TF (2.16 mg), ITIC-4F (1.26 mg, 0.84 μmol), and 10 (0.90 mg, 0.84 μmol) were dissolved in a PhCl:1,8-diiodooctane (99.5:0.5 v/v) solvent mixture (216 μL).

All reactions were set up in an argon-filled glovebox using anhydrous solvents in an identical procedure to the photovoltaic active layer solution preparation. Unless otherwise noted, all reactions were stirred for 24 h at 50 °C in an argon-filled glovebox and then were cooled to r.t. and then solvent was promptly removed under reduced pressure. The residue was further dried under vacuum (<25 mTorr) for 1 h and then dissolved in CD$_2$Cl$_2$ (0.75 mL) for NMR analysis (see Figures S21–S23).

**Note:** For NMR spectral evidence of end-group redistribution under light-free conditions, see Figure S16.
Figure S21. $^{19}$F-$^1$H NMR stack spectra of the reaction mixtures compared with purified compounds. Note that the formation of ITIC-4F in reaction B and C is likely due to self-scrambling of the generated ITIC-2F.
Figure S22. $^{13}$C NMR stack spectra of the reaction mixtures compared with purified compounds showing the region containing the enriched olefinic carbon signal. Shifts assignable to $\text{ITIC}^{(13\text{C})}-n\text{F}$ molecules are largely absent from the reaction mixture spectra.
Figure S23. $^1$H NMR spectra showing aldehyde region (left) and $^{19}$F{$^1$H} NMR spectra (right) of the reaction mixtures. Reactions A, B, and C exhibit significant reaction progress evident from the $^{19}$F{$^1$H} NMR spectra, however negligible singlet aldehyde signal at $\delta$ 9.89 ppm is present in the final mixture, indicating that aldehydic hydrogen atoms remain nearly exclusively bonded to $^{13}$C atoms resulting in the retention of the doublet aldehyde signal with peaks at $\delta$ 10.03 and 9.74 ppm ($J_{H-C} \approx 179$ Hz for both $^{13}$CHO-IDTT($^{13}$C)-0F and $^{13}$CHO-IDTT($^{13}$C)-2F). The greater reaction progress seen in Reaction C versus Reaction B is attributed to the higher dielectric constant of the ‘wet’ solvent mixture (see also Figure S20). Reaction D exhibits lower reaction progress, consistent with the slower exchange rate between ITIC-6F and ITIC-0F (see also Table S11). Reaction E exhibits no reaction progress by $^{19}$F{$^1$H} NMR or $^1$H NMR.
12. Grazing Incidence Wide-Angle X-Ray Scattering (GIWAXS) Measurements

The ITIC-\(n\)F pristine films were spun cast on Si/ZnO substrates from PhCl:1,8-diiodooctane (99.5:0.5 v:v) solutions (10 mg mL\(^{-1}\) concentration) and blend films were prepared exactly as the PV blend films and also spun onto Si/ZnO. GIWAXS measurements were performed at beamline 8ID-E at the Advanced Photon Source at Argonne National Laboratory. The samples were irradiated at incidence angles from 0.130° to 0.140° in vacuum at 10.915 keV for two summed exposures of 2.5 s each. Signals were collected with a Pilatus 1M detector located at a distance of 228.165 mm from the samples.

### Table S12. GIWAXS data for the pristine ITIC-\(n\)F acceptors and donor polymer films.

<table>
<thead>
<tr>
<th>Film</th>
<th>In-plane</th>
<th>Out-of-plane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lamellar d-spacing (Å)</td>
<td>Lamellar crystallite size (nm)</td>
</tr>
<tr>
<td>ITIC-0F</td>
<td>19.2</td>
<td>6.7</td>
</tr>
<tr>
<td>ITIC-2F</td>
<td>19.1</td>
<td>7.0</td>
</tr>
<tr>
<td>ITIC-4F</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ITIC-3F</td>
<td>19.2</td>
<td>5.4</td>
</tr>
<tr>
<td>ITIC-6F</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PBDB-TF</td>
<td>21.2</td>
<td>10.3</td>
</tr>
</tbody>
</table>
Figure S24. (Top) 2D GIWAXS patterns of the pristine material films. (Bottom) GIWAXS line cuts of the pristine material films showing the in-plane (IP, $q_{xy}$) and out-of-plane (OOP, $q_z$) crystalline scattering peaks.
Figure S25. GIWAXS line cuts of the PBDB-TF:ITIC-nF BHJ blend films showing the in-plane (IP, q_{xy}) and out-of-plane (OOP, q_z) crystalline scattering peaks. 2D data are in Figure 7.
Table S13. Summary of GIWAXS data for the binary and ternary photovoltaic BHJ blend films.

<table>
<thead>
<tr>
<th>Film</th>
<th>In-plane</th>
<th></th>
<th>Out-of-plane</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lamellar d-spacing (Å)</td>
<td>Lamellar crystallite size (nm)</td>
<td>Lamellar d-spacing (Å)</td>
<td>Lamellar crystallite size (nm)</td>
</tr>
<tr>
<td>ITIC-0F</td>
<td>21.2</td>
<td>13.4</td>
<td>19.2</td>
<td>11.5</td>
</tr>
<tr>
<td>ITIC-2F</td>
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<td>14.8</td>
<td>18.8</td>
<td>10.5</td>
</tr>
<tr>
<td>ITIC-2F SCR</td>
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<td>19.1</td>
<td>10.9</td>
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<tr>
<td>ITIC-4F</td>
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<td>13.3</td>
<td>18.9</td>
<td>10.0</td>
</tr>
<tr>
<td>ITIC-3F SCR</td>
<td>21.1</td>
<td>15.5</td>
<td>18.4</td>
<td>11.4</td>
</tr>
<tr>
<td>ITIC-6F</td>
<td>21.1</td>
<td>16.0</td>
<td>18.9</td>
<td>11.0</td>
</tr>
<tr>
<td>ITIC-0F: ITIC-4F</td>
<td>21.0</td>
<td>16.0</td>
<td>18.4</td>
<td>11.5</td>
</tr>
<tr>
<td>ITIC-0F: ITIC-4F SCR</td>
<td>20.9</td>
<td>14.4</td>
<td>19.1</td>
<td>11.1</td>
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<tr>
<td>ITIC-0F: ITIC-6F</td>
<td>21.0</td>
<td>15.1</td>
<td>18.3</td>
<td>10.8</td>
</tr>
<tr>
<td>ITIC-0F: ITIC-6F SCR</td>
<td>21.0</td>
<td>14.9</td>
<td>18.5</td>
<td>10.7</td>
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</tbody>
</table>
13. Atomic Force Microscopy (AFM)

AFM measurements were taken on a Dimension Icon scanning probe microscope (Bruker) in standard tapping mode. The blend thin films used were prepared in the same way as the optimized photovoltaic devices and spun cast on Si/ZnO substrates. Pristine ITIC-\(n\)F films were spun cast on Si/ZnO substrates from PhCl:1,8-diiodooctane (99.5:0.5 v:v) solutions (15 mg mL\(^{-1}\) concentration). The \(R_q\) values of the height images were obtained from the whole scan area.

Figure S26. AFM topographical (top) and phase (bottom) images of the pristine material films.
Figure S27. AFM topographical (top) and phase (bottom) images of the binary PBDB-TF:ITIC-nF BHJ films.

Figure S28. AFM topographical (top) and phase (bottom) images of the ternary PBDB-TF:ITIC-nF BHJ films.
14. SCLC Mobility Measurements

Hole-only diodes were fabricated using the structure: ITO/MoO$_x$ (9 nm)/active layer/MoO$_x$ (9 nm)/Ag (100 nm). Electron-only diodes were fabricated using the structure: ITO/ZnO (22 nm)/active layer/LiF (1 nm)/Al (100 nm). ITO was the hole injection electrode for the hole-only diodes, and Al was the electron injection electrode for the electron-only diodes. Both hole-only and electron-only diodes were measured in air. The PBDB-TF:ITIC-nF films were prepared in the same way as for the optimized PSC devices and film thickness are ~100–120 nm (Section 9 in SI). Pristine ITIC-nF films were spun cast from PhCl:1,8-diiodooctane (99.5:0.5 v:v) solutions (15 mg/mL concentration). The SCLC mobility was derived by fitting the $J$–$V$ curve in the space charge limited regime following Equation 3.$^{18}$

$$J = \frac{9}{8} \varepsilon_s \frac{V_{eff}^2}{d^3} \mu_0 \exp \left(0.89 \gamma \sqrt{\frac{V_{eff}}{d}}\right)$$

(Equation 3)

Here, $J$ is the current density, the parameter $\gamma$ describes the field dependence of the current, $\mu_0$ is the zero-field mobility, $\varepsilon_s$ and $d$ are the semiconductor permittivity (taken as $3\varepsilon_0$)$^{19}$ and organic film thickness (measured by Veeco Dektak 8 profilometer), respectively. The $V_{eff}$ was calculated by correcting the applied voltage ($V_{appl}$) for the series resistance of the ITO (20 $\Omega$/sq) and the built-in voltage ($V_{bi}$) of the device: $V_{eff} = V_{appl} - V_{bi} - V_{RS}$, where $V_{RS} = JAR_{series}$. For hole-only diodes $V_{bi} = 0$ V, and for electron-only devices $V_{bi} = 0.1$ V. Device dimensions were 200 $\mu$m × 200 $\mu$m with an area ($A$) of $4 \times 10^{-8}$ m$^2$. SCLC zero-field mobilities are reported as averages taken over 3 or more separate devices ± one standard deviation (1σ).

Figure S29. SCLC electron and hole mobilities for the pristine materials (left) and blend films (right).
Table S14. SCLC electron and hole mobilities for the pristine materials and blend films.

<table>
<thead>
<tr>
<th>Film</th>
<th>Film thickness (nm)</th>
<th>$\mu_h \times 10^4$ (cm²V⁻¹s⁻¹)</th>
<th>$\mu_e \times 10^4$ (cm²V⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITIC-0F</td>
<td>51</td>
<td>–</td>
<td>3.7 ± 2.6</td>
</tr>
<tr>
<td>ITIC-2F</td>
<td>54</td>
<td>–</td>
<td>3.0 ± 2.1</td>
</tr>
<tr>
<td>ITIC-4F</td>
<td>52</td>
<td>–</td>
<td>5.1 ± 4.0</td>
</tr>
<tr>
<td>ITIC-3F</td>
<td>45</td>
<td>–</td>
<td>4.4 ± 2.8</td>
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<tr>
<td>ITIC-6F</td>
<td>57</td>
<td>–</td>
<td>5.7 ± 2.2</td>
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<tr>
<td>PBDB-TF</td>
<td>54</td>
<td>6.9 ± 1.7</td>
<td>–</td>
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<td>PBDB-TF : ITIC-0F</td>
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<td>2.7 ± 1.0</td>
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<td>1.3 ± 1.0</td>
<td>2.0 ± 0.3</td>
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<td>PBDB-TF : ITIC-2F SCR</td>
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<td>4.7 ± 1.9</td>
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<tr>
<td>PBDB-TF : ITIC-4F</td>
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<td>4.5 ± 2.0</td>
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<td>PBDB-TF : ITIC-0F : ITIC-4F SCR</td>
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<td>8.0 ± 3.5</td>
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</tr>
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15. References


