Boron-Nitrogen Substituted Dihydroindeno[1,2-b]fluorene Derivatives as Acceptors in Organic Solar Cells.

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Table of Contents

General Considerations	S2
Synthetic Procedures	S3
Organic Solar Cell Procedures	S9
Computational Details	S11
Figure S1: Molecular structure of 1-Cl	S12
Figure S2: Frontier molecular orbitals and TD-DFT calculated UV-Vis absorption profile for 1-Tol	S12
Figure S3: Cyclic voltammogram of 1-Cl	S13
Figure S4: Cyclic voltammogram of 2-Cl	S13
Figure S5: Cyclic voltammogram of 1-FAr	S14
Figure S6: Cyclic voltammogram of 1-FAr	S14
Figure S7: Cyclic voltammogram of 1-Tol	S15
Figure S8: Cyclic voltammogram of 1-Tol	S15
Figure S9: Cyclic voltammogram of 2-FAr	S16
Figure S10: Cyclic voltammogram of 2-Tol	S16
Table S1: Collected electrochemical data for all compounds	S17
Figure S11: A) Chemical structures of donor polymers used in this study, B) Device architecture, C) Current density- voltage curves for best polymer: 1-FAr based organic solar cells.	S18
Figure S12: Energy level diagrams for PTB7-Th, PBDB-T, PPDT2FBT, 1-FAr, 2-FAr, 1-Tol, and 2-Tol	S19
Figure S13: Optical spectra for PTB7-Th:1-FAr, PBDB-T:1-FAr, and PPDT2FBT:1-	S20

FAr blended films on glass/ZnO. A-C) absorption spectra D-F) photoluminescence	
spectra.	
Figure S14: Atomic force microscopy images (5x5 μ m) for PTB7-Th:1-FAr, PBDB- T:1-FAr ₂ , and PPDT2FBT:1-FAr based organic solar cells. A-C) Height images and D-	S21
F) phase images. The organic surface was mapped in-between the top electrodes.	000
Figure S15: UV-Vis absorption and emission spectra of I-CI	822
Figure S16: UV-Vis absorption and emission spectra of 1-Cl, 1-Far, and 1-Tol	S22
Figure S17: UV-Vis absorption spectra of Cl, Far, and Tol derivatives	S23
Figure S18: UV-Vis absorption and emission spectra of 2-Pz.	S23
Figure S19: UV-Vis absorption spectra of 1-Cl, 1-FAr, and 1-Tol derivatives in	S24
dichloromethane solutions, plotted as molar absorptivity against wavelength.	
Figure S20: UV-Vis absorption spectra of 2-Cl, 2-FAr, and 2-Tol derivatives in	S24
dichloromethane solutions, plotted as molar absorptivity against wavelength	
Figure S21: Frontier molecular orbitals and TD-DFT (PBE0/def-TZVP) calculated UV-	S25
Vis absorption profile for 1-FAr , with transitions highlighted in colours.	
Figure S22: ¹ H NMR (top) and ¹³ C NMR(bottom) spectra of 1-Pz.	S26
Figure S23: ¹ H NMR (top) and ¹³ C NMR(bottom) spectra of 2-Pz.	S27
Figure S24: ¹ H NMR (top) and ¹³ C NMR(bottom) spectra of 1-Cl.	S28
Figure S25: ¹ H NMR (top) and ¹³ C NMR(bottom) spectra of 2-Cl.	S29
Figure S26: ¹ H NMR (top) and ¹³ C NMR(bottom) spectra of 1-FAr.	S30
Figure S27: ¹ H NMR (top) and ¹³ C NMR(bottom) spectra of 1-Tol.	S31
Figure S28: ¹ H NMR (top) and ¹³ C NMR (bottom) spectra of 2-FAr.	S32
Figure S29: ¹ H NMR (top) and ¹³ C NMR (bottom) spectra of 2-Tol	S33
Table S2: Organic solar cell data for devices using active layers comprised of PTB7-	S34
Th:1-FAr, PBDB-T:1-FAr, PPDT2FBT:1-FAr.	
Table S3: Average solar cell data for devices using active layers comprised of PTB7-	S35
Th:1-FAr	
Table S4: Average organic solar cell data for devices using active layers comprised of	S35
PTB7-Th:1-Tol, PTB7-Th:2-Tol, PTB7-Th:1-FAr, and PTB7-Th:2-FAr.	aa -
Keterences	\$35

General Considerations: All experiments were performed under a purified argon atmosphere either using a MBraun Unilab glove box or a double manifold high vacuum line following standard techniques, unless otherwise specified. Hexanes, pentane, diethyl ether and tetrahydrofuran were dried and purified using a Grubbs/Dow solvent purification system and stored in 500ml thick-walled Kontes flasks over sodium/benzophenone ketal. Dichloromethane

and chlorobenzene were stored in the same manner except dried over calcium dihydride instead of sodium/benzophenone ketal. All dried solvents were degassed and vacuum distilled prior to use. All other commercially available starting materials were used without further purification. $Zn(C_6F_3H_2)_2$, $Zn(p-Tol)_2$, and bis(4-tButylphenyl)aminophenylboronic acid was prepared as previously reported.¹ NMR were obtained using either a BrukerRDQ-400, Bruker Ascend-500, or Bruker Avance-600 MHz NMR spectrometer with solvent peaks referenced to tetramethylsilane as an internal standard for ¹H and ¹³C. UV-Vis fluorescence data was collected using a Horiba FluoroMax-4 spectrometer. Fluorescence spectra were recorded in dichloromethane solutions, and excited at the highest wavelength absorption maxima for each compound. Absolute fluorescence quantum yield values were measured using an Edinburgh Instruments FLS92 calibrated integrating sphere S 3 system. Cyclic voltammetry was collected with a CHI660D potentiostat using a three electrode setup using a CHI660D potentiostat. Glassy carbon, platinum wire, and silver wire were used as the working, counter, and reference electrodes, respectively. Ionic strength of the solution was maintained by using a 0.1M solution of [nBu₄N][PF₆] in THF solvent. All cyclic voltammograms were referenced to the Fc/Fc⁺ couple. The energies for E_{ox} and E_{red} used for estimating the HOMO and LUMO energy levels were calculated using the onset potential of reduction or oxidation.



Synthesis of tBuPyrazine 1-Pz:

Synthesis adapted from Williams et al.² 4-tButylphenylboronic acid (4.45g, 25.0 mmol) and 2,5dibromopyrazine (2.29g, 9.6 mmol) were dissolved in 1,4-dioxane (75mL) and the mixture degassed by bubbling through argon for 10 minutes. A solution of K₂CO₃ (7.96g, 57.6 mmol) in 25 mL of water and tetrakis(triphenylphosphine)palladium (6%, 666mg, 0.58 mmol) were added and the reaction mixture was again degassed for 10 minutes. The reaction was heated at 95C for 16 hours. Upon cooling a solid precipitated which was collected by filtration. The solid was then recrystallized form hot ethanol yielding 2,5-di(4-*t*Buphenyl)pyrazine (2.76g, 8.0 mmol, 83% yield). ¹H NMR (500 MHz, CDCl₃) δ 9.06 (s, 2H), 8.01 (d, *J* = 8.5 Hz, 4H), 7.56 (d, *J* = 8.5 Hz, 4H), 1.39 (s, 18H). ¹³C NMR (126 MHz, CDCl₃) δ 152.43, 149.75, 140.47, 132.97, 125.87, 125.47, 34.25, 30.69. Elemental Analysis: Calculated C 83.68 H 8.19 N 8.13, Found C 83.25 H 8.01 N 7.98.



Synthesis of tBuPyrazine 2-Pz:

Synthesis adapted from Williams et al.² bis(4-*t*Butylphenyl)aminophenylboronic acid (630mg, 1.6 mmol) and 2,5-dibromopyrazine (150mg, 0.63 mmol) were dissolved in 1,4-dioxane (30mL) and the mixture degassed by bubbling through argon for 10 minutes. A solution of K₂CO₃ (520mg, 3.76 mmol) in 5 mL of water and tetrakis(triphenylphosphine)palladium (6%, 43 mg, 0.04 mmol) were added and the reaction mixture was again degassed for 10 minutes. The reaction was heated at 95C for 16 hours. Upon cooling a bright yellow solid precipitated which was collected by filtration. The solid was then recrystallized form hot ethanol yielding 2,5-di(bis4-*t*Buphenylaminophenyl)pyrazine (452mg, 0.56 mmol, 91% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.95 (s, 2H), 7.89 (d, *J* = 8.8 Hz, 4H), 7.30 (d, *J* = 8.7 Hz, 8H), 7.14 (d, *J* = 8.8 Hz, 4H), 7.09 (d, *J* = 8.6 Hz, 8H), 1.33 (s, 36H). ¹³C NMR (126 MHz, CDCl₃) δ 148.97, 148.82,

145.89, 143.87, 139.82, 128.22, 126.65, 125.61, 124.08, 121.29, 33.79, 30.86. Elemental Analysis: Calculated C 85.02 H 7.90 N 7.08. Found C 85.31 H 7.54 N 7.23.



Synthesis adapted from Ingleson et al³. A two neck round bottom flask was charged with 1-Pz (400mg, 1.16mmol) and tri-tert-butylpyridine (574 mg, 2.32 mmol), and dichloromethane (50mL) was added via vacuum transfer. A solution of borontrichloride in dichloromethane (1.0M, 2.9 mL) was slowly added and the colour changed from clear and colourless to a bright orange. Solid aluminum chloride (619mg, 4.64 mmol) was added to the flask causing an immediate colour change to dark purple. This was stirred at room temperature for 16 hours, before tetramethylammonium chloride (254mg, 2.32 mmol) was added and allowed to stir for 1 hour. The solvent was then removed in vacuo yielding a dark orange solid. Water was added to the flask turing the solid a brighter orange colour and the product was collected by filtration before being washed with more water (150 mL) and hexanes (150 mL) before being dried under high vac yielding a bright orange solid 1-Cl (510 mg, 1.0 mmol, 87% yield). ¹H NMR (500 MHz, CDCl₃) δ 9.26 (s, 2H), 7.90 (d, J = 1.8 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 7.59 (dd, J = 8.2, 1.8 Hz, 2H), 1.42 (s, 18H). ¹³C NMR (126 MHz, CDCl₃) δ 159.12, 149.61, 134.26, 127.46, 127.29, 126.92, 122.19, 35.31, 30.56.(Carbon attached to boron not observed) ¹¹B NMR (161 MHz, CDCl₃) δ 8.39. Elemental Analysis: Calculated C 56.98 H 5.18 N 5.54, Found C 57.27 H 5.26 N 5.44.



Synthesis of 2-Cl:

Synthesis adapted from Ingleson et al. A two neck round bottom flask was charged with 2-Pz (500mg, 0.63mmol) and tri-tert-butylpyridine (313 mg, 1.26 mmol), and dichloromethane (50mL) was added via vacuum transfer. A solution of borontrichloride in dichloromethane (1.0M, 1.6 mL) was slowly added and the colour changed from fluorescent yellow to dark purple. Solid aluminum chloride (340mg, 2.53 mmol) was added to the flask causing a colour change to darker purple-blue. This was stirred at room temperature for 16 hours, before tetramethylammonium chloride (275mg, 2.51 mmol) was added and allowed to stir for 1 hour. The solvent was then removed in vacuo yielding a dark green solid. Water was added to the flask turning the solid a brighter green colour and the product was collected by filtration before being washed with more water (150 mL) and hexanes (150 mL) before being dried under high vac vielding a dark green solid **2-Cl** (402 mg, 0.42 mmol, 68% vield). ¹H NMR (500 MHz, CDCl₃) δ 8.80 (s, 2H), 7.47 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.6 Hz, 8H), 7.34 (d, J = 2.3 Hz, 2H), 7.13 (d, J = 8.6 Hz, 8H), 6.91 (dd, J = 8.7, 2.3 Hz, 2H), 1.35 (s, 36H). ¹³C NMR (126 MHz, CDCl₃) δ 153.12, 148.05, 146.39, 142.35, 133.47, 126.10, 125.59, 122.90, 121.19, 119.30, 118.86, 33.99, 30.82.(Signal for carbon attached to boron not observed). ¹¹B Signal not observed. Elemental Analysis: Calculated: C 70.61 H 6.35 N 5.88. Found C 70.55 H 6.30 N 5.91.



A round bottom flask was charged with **1-Cl** (103mg, 0.20mmol) and Zn(C₆H₂F₃)₂ (167 mg, 0.51 mmol) and dichloromethane (20mL). The solution immediately turned a bright fluorescent yellow colour and was stirred at room temperature for 10 minutes. The solution was then passed through a silica plug with dichloromethane and the dried under high vacuum yielding **1-FAr** as a bright orange solid (134 mg, 0.42 mmol, 74% yield). ¹H NMR (500 MHz, CDCl₃) δ 9.24 (s, 2H), 7.84 (d, *J* = 1.7 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.45 (dd, *J* = 8.3, 1.8 Hz, 2H), 6.52 (t, *J* = 8.5 Hz, 8H), 1.33 (s, 18H). ¹³C NMR (126 MHz, CDCl₃) δ 164.81(dt, ¹*J*_{CF} = 243 Hz, ³*J*_{CF} = 17 Hz) 161.47(dt, ¹*J*_{CF} = 247 Hz, ³*J*_{CF} = 17 Hz), 159.25, 156.22, 150.56, 135.38, 128.66, 127.23, 124.28, 120.85, 114.77(br), 99.47(dd, ²*J*_{CF} = 34 Hz, ²*J*_{CF} = 24 Hz), 34.88, 30.59. (Signal for carbon attached to boron on phenylpyrazine core not observed). ¹¹B NMR (161 MHz, CDCl₃) δ 0.15. (Elemental Analysis: Calculated C 64.89 H 3.86 N 3.15. Found C 65.10 H 4.18 N 3.09.



A round bottom flask was charged with **1-Cl** (77mg, 0.15mmol), Zn(*p*tol)₂ (94 mg, 0.38 mmol) and dichloromethane (20mL). The solution immediately turned a dark yellow colour and was stirred at room temperature for 10 minutes. The solution was then passed through a silica plug

with dichloromethane and the dried under high vacuum yielding **1-Tol** as a dark yellow solid (58 mg, 0.08 mmol, 53% yield). ¹H NMR (500 MHz, CDCl₃) δ 9.05 (s, 2H), 7.78 (d, *J* = 1.8 Hz, 2H), 7.75 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.20 – 7.14 (m, 8H), 7.13 – 7.07 (m, 8H), 2.33 (s, 12H), 1.34 (s, 8H). ¹³C NMR (126 MHz, CDCl₃) δ 163.09(br), 155.55, 149.90, 144.58 (br), 135.44, 134.37, 132.49, 129.60, 128.17, 127.13, 123.88, 34.90, 30.75, 20.65. (signal for carbon attached to boron on phenylpyrazine not observed), ¹¹B NMR (161 MHz, CDCl₃) δ 6.34 Elemental Analysis: Calculated C 85.72 H 7.47 N 3.84. Found C 85.70 H 7.40 N 3.66.



A round bottom flask was charged with **2-Cl** (60mg, 0.06mmol) and $Zn(C_6H_2F_3)_2$ (52 mg, 0.16 mmol) and dichloromethane (20mL). The solution immediately turned a darker green colour, and all the insoluble **2-Cl** went into solution. The reaction was stirred at room temperature for 10 minutes. The solution was then passed through a silica plug with dichloromethane and then dried under high vacuum yielding **2-FAr** as a dark green solid (61 mg, 0.05 mmol, 75% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.86 (s, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 2.1 Hz, 2H), 7.26 (d, *J* = 9.1 Hz, 8H), 7.01 (d, *J* = 8.6 Hz, 8H), 6.90 – 6.84 (m, 2H), 6.47 (t, *J* = 8.3 Hz, 8H), 1.32 (s, 36H). ¹³C NMR (126 MHz, CDCl₃) δ 164.74(dt, ¹*J*_{CF} = 246 Hz, ³*J*_{CF} = 15 Hz), 161.44 (dt, ¹*J*_{CF} = 248 Hz, ³*J*_{CF} = 15 Hz), 151.52, 148.33, 146.65, 143.22, 134.72, 125.54, 124.56, 123.78, 121.67, 121.27, 115.15 (br), 99.23(dd, ²*J*_{CF} = 34 Hz, ²*J*_{CF} = 25 Hz), 33.83, 30.81. (Signals for carbon attached to boron are not observed). ¹¹B Signal not observed. Elemental Analysis: Calculated C 71.97 H 5.13 N 4.20. Found C 72.10 H 5.12 N 3.99.



A round bottom flask was charged with **2-Cl** (80mg, 0.08mmol) and $Zn(ptol)_2$ (52 mg, 0.21 mmol) and dichloromethane (20mL). The solution immediately turned a darker green colour, and all the insoluble **2-Cl** went into solution. The reaction was stirred at room temperature for 10 minutes. The solution was then passed through a silica plug with dichloromethane and then dried under high vacuum yielding **2-Tol** as a dark green solid (52 mg, 0.05 mmol, 55% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.73 (s, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 2.2 Hz, 2H), 7.26 (d, *J* = 1.9 Hz, 8H), 7.12 (d, *J* = 7.9 Hz, 8H), 7.08 – 7.02 (m, 16H), 6.85 (dd, *J* = 8.6, 2.2 Hz, 2H), 2.32 (s, 12H), 1.33 (s, 36H). ¹³C NMR (126 MHz, CDCl₃) δ 163.95, 151.03, 147.74, 146.47, 144.95, 143.47, 135.21, 133.69, 132.43, 128.00, 125.60, 124.71, 122.01, 121.35, 118.60, 33.83, 30.85, 20.66.(¹³C signal attached to B not observed). ¹¹B Signal not observed. Elemental Analysis: Calculated C 85.85 H 7.55 N 4.77. Found C 85.65 H 7.30 N 4.88.

Device Methods:

Materials: PTB7-Th (lot# YY13258CH) used in this study was purchased from 1- Material. PBDB-T (Batch No: P1-147-2) and PPDT2FBT (Batch No: BM3-135) used in this study are commercially available and were provided to us by Brilliant Matters.

UV-Visible Spectroscopy (UV-Vis): All optical absorption measurements were recorded using Agilent Technologies Cary 60 UV-Vis spectrometer at room temperature. All solution UV-Vis experiments were run in CHCl₃ using 10 mm quartz cuvettes. Films were spin-cast into Corning glass micro slides from C_6H_5Cl solutions (10mg/mL) at 1000 rpm. Prior to use, glass slides were

cleaned with soap and water, acetone and isopropanol, and followed by UV/ozone treatment using a Novascan UV/ozone cleaning system.

Photoluminescence (PL): All emission measurements were recorded using an Agilent Technologies Cary Eclipse fluorescence spectrophotometer at room temperature.

Atomic Force Microscopy (AFM): AFM measurements were performed by using a TT2- AFM (AFM Workshop) in tapping mode and WSxM software with a resonance frequency of 300 kHz, a force constant of 40 N/m and a reflective back side aluminum coating (Tap300Al-G, BudgetSensors). Samples for AFM measurements were the same ones that were used to collect the respective device parameters.

OSC Fabrication: Devices were fabricated using ITO-coated glass substrates cleaned by sequentially ultra-sonicating detergent and de-ionized water, acetone, and isopropanol followed by exposure to UV/ozone for 30 minutes. ZnO was subsequently deposited as a sol-gel precursor solution in the air following the method of Sun et al.¹. The room temperature solution was filtered and spin-cast at a speed of 4000 rpm and then annealed at 200 °C in air for 15 min. Solutions of polymers was stirred at 70 °C for 4-6 hrs. Active layer solutions were prepared in the air using C₆H₅Cl as the casting-solvent. Then, active layer materials were combined in a proper donor/acceptor weight ratio and cast at room temperature and spin-coated (1000 rpm) onto the glass/ITO/ZnO in air at room temperature. After spin-casting the active layers the substrates/films were kept in an N₂ atmosphere glovebox overnight to dry before evaporating MoO_x and Ag. A 10 nm layer of MoO_x followed by a 100 nm layer of Ag was thermally deposited under vacuum (3x10⁻⁶ Torr) using a shadow mask. The device size was 0.09 cm².

OSC Testing: The current density-voltage (J-V) curves were measured by a Keithley 2420 source measure unit. The photocurrent was measured under AM 1.5 illumination at 100 mW/cm^2 under a Solar Simulator (Newport 92251A-1000). The standard silicon solar cell (Newport 91150V) was used to calibrate light intensity.

Computational Details

Geometries of minimum structures and transition states were optimized with Gaussian 09 program package ^{C1} using PBE0 hybrid density functional ^{C2} and Ahlrichs' small triple- ζ valence quality def-TZVP basis sets.^{C3} Nature of the stationary points was ascertained by frequency calculations and none of the optimized structures showed negative eigenfrequencies. Electronic excitation energies and oscillation strengths for the transitions were calculated using the time-dependent density functional formalism (TDDFT)^{C4} on optimized structures.

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Supplementary Figures:



Figure S 1: Molecular structure of 1-Cl. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) B(1)-N(1) 1.615(6), B(1)-C(1) 1.582(6), C(1)-C(2) 1.399(5), C(2)-C(3) 1.432(5), C(3)-C(4) 1.396(5), N(1)-C(3) 1.368(4), N(1)-C(5) 1.304(5).



Figure S 2: Frontier molecular orbitals and TD-DFT calculated UV-Vis absorption profile **for 1-Tol**, with transitions highlighted in colours. The experimental UV-Vis spectra is overlaid for comparison.



Figure S 3: Cyclic voltammetry of a solution of **1-Cl** in THF was measured using a three electrode setup using a CHI660D potentiostat. Glassy carbon, platinum wire, and silver wire were used as the working, counter, and reference electrodes, respectively. Ionic strength of the solution was maintained by using a 0.1 M solution of [nBu₄N][PF₆] in THF solvent. The current was swept in the negative direction with a sweep window from -0.9 V to 2.3 V at 100 mV/s.



Figure S 4: Cyclic voltammetry of a solution of **2-Cl** in THF was measured using a three electrode setup using a CHI660D potentiostat. Glassy carbon, platinum wire, and silver wire

were used as the working, counter, and reference electrodes, respectively. Ionic strength of the solution was maintained by using a 0.1 M solution of [nBu₄N][PF₆] in THF solvent. The current was swept in the negative direction with a sweep window from -1.8 V to 1.2 V at 100 mV/s.



Figure S 5: Cyclic voltammetry of a solution of **1-FAr** in THF was measured using a three electrode setup using a CHI660D potentiostat. Glassy carbon, platinum wire, and silver wire were used as the working, counter, and reference electrodes, respectively. Ionic strength of the solution was maintained by using a 0.1 M solution of $[nBu_4N][PF_6]$ in THF solvent. The current was swept in the negative direction with a sweep window from -1.3 V to -0.3 V at 100 mV/s.



Figure S 6: Cyclic voltammetry of a solution of **1-FAr** in THF was measured using a three electrode setup using a CHI660D potentiostat. Glassy carbon, platinum wire, and silver wire

were used as the working, counter, and reference electrodes, respectively. Ionic strength of the solution was maintained by using a 0.1 M solution of [nBu₄N][PF₆] in THF solvent. The current was swept in the negative direction with a sweep window from -0.9 V to 1.9 V at 100 mV/s.



Figure S 7: Cyclic voltammetry of a solution of **1-Tol** in THF was measured using a three electrode setup using a CHI660D potentiostat. Glassy carbon, platinum wire, and silver wire were used as the working, counter, and reference electrodes, respectively. Ionic strength of the solution was maintained by using a 0.1 M solution of [nBu₄N][PF₆] in THF solvent. The current was swept in the negative direction with a sweep window from -1.4 V to -0.3 V at 100 mV/s.



Figure S 8: Cyclic voltammetry of a solution of **1-Tol** in THF was measured using a three electrode setup using a CHI660D potentiostat. Glassy carbon, platinum wire, and silver wire

were used as the working, counter, and reference electrodes, respectively. Ionic strength of the solution was maintained by using a 0.1 M solution of [nBu₄N][PF₆] in THF solvent. The current was swept in the negative direction with a sweep window from -0.9 V to 1.9 V at 100 mV/s.



Figure S 9: Cyclic voltammetry of a solution of **2-Far** in THF was measured using a three electrode setup using a CHI660D potentiostat. Glassy carbon, platinum wire, and silver wire were used as the working, counter, and reference electrodes, respectively. Ionic strength of the solution was maintained by using a 0.1 M solution of [nBu₄N][PF₆] in THF solvent. The current was swept in the negative direction with a sweep window from -2.2 V to 2.0 V at 100 mV/s.



Figure S 10: Cyclic voltammetry of a solution of **2-Tol** in THF was measured using a three electrode setup using a CHI660D potentiostat. Glassy carbon, platinum wire, and silver wire

were used as the working, counter, and reference electrodes, respectively. Ionic strength of the solution was maintained by using a 0.1 M solution of $[nBu_4N][PF_6]$ in THF solvent. The current was swept in the negative direction with a sweep window from -2.2 V to 2.0 V at 100 mV/s.

Species	Reduction (V)	Oxidation (V)
1-Cl	-0.51	1.75, 1.89
2-Cl	-0.78, -1.41	0.55, 0.75
1-FAr	-0.95	1.61
1-Tol	-1.19	1.31
2-FAr	-1.21	0.51, 0.69, 1.60
2-Tol	n/a	0.44, 0.71

Table S 1: Collected electrochemical reduction and oxidation potentials, with potentials given for $E_{1/2}$. All values are referenced to the Fc/Fc⁺ couple.

2. Organic Solar Cell Data (Polymer:1-FAr)



Figure S 11: A) Chemical structures of donor polymers used in this study, B) Device architecture, C) Current density- voltage curves for best polymer: **1-FAr** based organic solar cells.



Figure S 12: A) energy level diagram for PTB7-Th, PBDB-T, PPDT2FBT, and **1-FAr**. Energy levels for **1-FAr** are determined by solution cyclic voltammetry B) Chemical structures of PTB7-Th, PBDB-T, PPDT2FBT, and **1-FAr**. C) Energy level diagram for PTB7-Th, **1-FAr**, **2-FAr**, **1-Tol**, and **2-Tol**. Energy levels for **1-FAr**, **2-FAr**, **1-Tol**, and **2-Tol** are determined by solution cyclic voltammetry. D) Chemical structures for PTB7-Th, **1-FAr**, **2-FAr**, **1-Tol**, and **2-Tol**, and **2-Tol**.



Figure S 13: Optical spectra for PTB7-Th:1-FAr, PBDB-T:1-FAr, and PPDT2FBT:1-FAr blended films on glass/ZnO. A-C) absorption spectra D-F) photoluminescence spectra.



Figure S 14: Atomic force microscopy images (5x5 μ m) for PTB7-Th:1-FAr, PBDB-T:1-FAr, and PPDT2FBT:1-FAr based organic solar cells. A-C) Height images and D-F) phase images. The organic surface was mapped in-between the top electrodes.



Figure S 15. UV-Vis absorption and emission spectra of 1-Cl in a dichloromethane solution.



Figure S 16: UV-Vis absorption and emission spectra of **1-Cl**, **1-FAr**, and **1-Tol** in a dichloromethane solution



Figure S17: UV-Vis absorption spectra of Cl, FAr, and Tol derivatives in dichloromethane solutions.



Figure S 18: UV-Vis absorption and emission spectra of **2-Pz** in a dichloromethane solution.



Figure S 19: UV-Vis absorption spectra of 1-Cl, 1-FAr, and 1-Tol derivatives in dichloromethane solutions, plotted as molar absorptivity against wavelength.



Figure S 20: UV-Vis absorption spectra of **2-Cl**, **2-FAr**, and **2-Tol** derivatives in dichloromethane solutions, plotted as molar absorptivity against wavelength.



Figure S21: Frontier molecular orbitals and TD-DFT (PBE0/def-TZVP) calculated UV-Vis absorption profile for **1-FAr**, with transitions highlighted in colours. The experimental UV-Vis spectra is overlaid for comparison.





Figure S 23: ¹H NMR (top) and ¹³C NMR(bottom) spectra of **2-Pz**.



Figure S 24: ¹H NMR (top) and ¹³C NMR(bottom) spectra of **1-Cl.**



Figure S 25: ¹H NMR (top) and ¹³C NMR(bottom) spectra of **2-Cl.**



Figure S 26: ¹H NMR (top) and ¹³C NMR(bottom) spectra of **1-FAr**.



Figure S 27: ¹H NMR (top) and ¹³C NMR(bottom) spectra of **1-Tol**.



Figure S 28: ¹H NMR (top) and ¹³C NMR (bottom) spectra of **2-Far**.



Blend	V _{OC} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
PTB7-Th:1-FAr	0.85	4.4	39	1.4
	0.83	4.1	39	1.3
	0.86	4.9	38	1.6
	0.87	5.1	41	1.8
	0.89	5.6	40	2.0
	0.87	5.9	39	2.0
	0.82	4.7	36	1.4
	0.81	4.5	35	1.3
	0.85	4.6	37	1.5
	0.83	4.5	38	1.4
	0.81	4.2	35	1.2
Average	0.85	4.8	38	1.5
PBDB-T:1-FAr	0.87	2.7	38	0.9
	0.86	2.7	39	0.9
	0.86	2.7	37	0.9
	0.86	2.7	36	0.8
	0.81	2.8	39	0.9
Average	0.85	2.7	38	0.9
PPDT2FBT:1-FAr	0.78	3.3	39	1.0
	0.78	3.4	39	1.1
	0.77	3.2	37	0.9
	0.78	3.6	39	1.1
Average	0.78	3.4	38	1.0
Device architecture = glass/ITO/ZnO/BHJ/MoO _x /Ag				
All active layers cast from 1:1 weight ratio C_6H_5Cl solutions with a total solid concentration of 10 mg/mL.				

Table S2. Organic solar cell data for devices using active layers comprised of PTB7-Th:**1-FAr**, PBDB-T:**1-FAr**, PPDT2FBT:**1-FAr**. Best results are highlighted in bold. Averages are in italics.

Ratio (D/A)	Additive / (v/v %)	V _{OC} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
7:3	-	0.83	4.5	35	1.3
3:7	-	0.84	3.6	37	1.1
1:1	DIO / 0.25	0.81	3.6	39	1.2
1:1	DIO / 0.50	0.83	3.9	39	1.3
1:1	DIO / 1.00	0.83	3.8	39	1.2
1:1	DIO / 3.00	0.75	2.9	36	0.9
1:1	CN / 0.50	0.84	4.5	38	1.4
1:1	CN / 1.00	0.83	4.3	38	1.4
1:1	CN / 3.00	0.81	4.1	37	1.2
1:1	CN / 5.00	0.82	4.2	38	1.3
1:1	DPE / 1.00	0.83	5.3	35	1.5
Device architecture = $glass/ITO/ZnO/BHJ/MoO_x/Ag$					
All active layers cast C_6H_5Cl solutions with a total solid concentration of 10 mg/mL.					
DIO - 1,8-diiodooctane, $CN = 1$ -chloronapthalene, $DPE = Diphenyl ether$					

 Table S3. Average solar cell data for devices using active layers comprised of PTB7-Th:1-FAr

Tables S4. Average organic solar cell data for devices using active layers comprised of PTB7-Th:**1-Tol**, PTB7-Th:**2-Tol**, PTB7-Th:**1-FAr**, and PTB7-Th:**2-FAr**

Blend	V _{OC} (V)	$\frac{J_{sc}}{(mA/cm^2)}$	FF (%)	PCE (%)
PTB7-Th:1-Tol	0.96	1.4	31	0.4
PTB7-Th:2-Tol	0.89	0.8	27	0.2
PTB7-Th:1-FAr	0.87	5.4	40	1.9
PTB7-Th:2-FAr	0.79	1.2	31	0.3
Device architecture = glass/ITO/ZnO/BHJ/MoO _x /Ag				
All active layers cast from 1:1 weight ratio C ₆ H ₅ Cl solutions with a total solid concentration of				
10 mg/mL.				

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