

## Electronic Supplementary Information

### Synthesis and Characterization of Solution Processable, High Electron Affinity Molecular Dopants

Jan Saska,<sup>‡</sup> Nikolay E. Shevchenko,<sup>‡</sup> Goktug Gonel,<sup>†</sup> Zaira I. Bedolla-Valdez,<sup>†</sup>  
Rachel M. Talbot,<sup>†</sup> Adam J. Moulé,<sup>\*,†</sup> and Mark Mascal<sup>\*,‡</sup>

<sup>‡</sup>Department of Chemistry, University of California Davis, Davis, CA, 95616 USA

<sup>†</sup>Department of Chemical Engineering, University of California Davis, CA, 95616 USA

#### Table of Contents

1	Dopant synthesis	S2
1.1	Materials and Methods	S2
1.2	<sup>1</sup> H and <sup>13</sup> C NMR Spectroscopy	S3
1.3	Dopant Cyclic Voltammetry	S9
2	Copolymer Synthesis	S12
2.1	Materials and Methods	S12
2.2	General Procedure	S12
2.3	VT <sup>1</sup> H NMR Spectroscopy of Polymers	S13
2.4	Polymer Cyclic Voltammetry	S17
3	Dopant Stability Measurements	S19
4	Additional References	S21

## 1 Dopant synthesis

### 1.1 Materials and Methods

#### General

Reagents and solvents were purchased from Millipore-Sigma with the following exceptions: nitrosonium tetrafluoroborate and tetrachlorocyclopropene were purchased from Acros Organics. Dichloromethane ( $\geq 99.5\%$ , inhibitor-free) and acetonitrile ( $\geq 99.8\%$  anhydrous, degassed and low oxygen) were purchased from Sigma-Aldrich. All commercially available solvents and reagents were used as supplied. Reactions were carried out under a dry argon atmosphere unless otherwise specified. Reaction heating was achieved using an oil bath and a stirrer-hotplate with an integrated thermocouple. Reaction cooling to temperatures up to  $0\text{ }^{\circ}\text{C}$  was achieved using an ice/water bath, and cooling to temperatures below  $0\text{ }^{\circ}\text{C}$  was achieved using an acetone/dry ice bath. Reactions were monitored using thin layer chromatography (TLC) on Sorbtech Silica XG TLC plates with a fluorescent indicator. Plates were visualized using ultraviolet light (254 nm) and/or  $\text{KMnO}_4$  solution, as appropriate.

Commercially available polymers were purchased: P3HT (MW: 50000-70000, Regioregularity  $\geq 90\%$ ) from Sigma-Aldrich and pDPP-4T from Ossila Ltd. The remaining polymers, pDPP-3T, pDPP-2T, and pDPPT2-T2F4, were synthesized by the Stille polycondensation method using the procedure given in the Electronic Supplementary Information.

400 MHz Bruker AVIIIHD and 600 MHz Varian VNMRS spectrometers were used to record  $^1\text{H}$  and  $^{13}\text{C}$  spectra of compounds in the indicated deuterated solvent. All chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to residual solvent peaks as follows:  $\text{CDCl}_3$  ( $\delta_{\text{H}} = 7.26$  ppm,  $\delta_{\text{C}} = 77.0$  ppm),  $\text{CD}_3\text{CN}$  ( $\delta_{\text{H}} = 1.94$  ppm,  $\delta_{\text{C}} = 118.3$  ppm). Coupling constants ( $J$ ) are averaged.  $^{13}\text{C}$  NMR spectra are  $^1\text{H}$  decoupled.

High resolution mass spectra (HRMS) were recorded on a Thermo Fisher Hybrid LTQ-Orbitrap XL mass spectrometer.

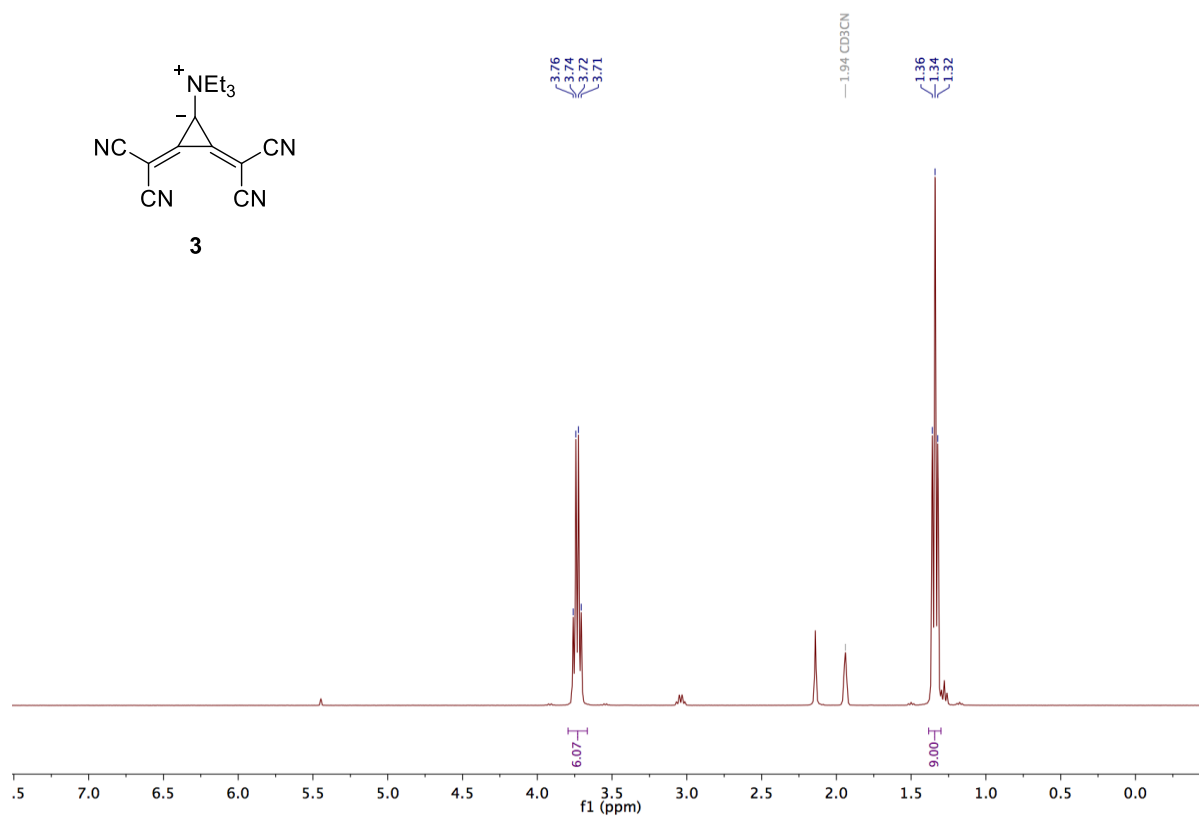
Cyclic voltammograms of the dopants were recorded on a BASi Epsilon MF-9092 electrochemical workstation. Redox potentials were measured in degassed anhydrous acetonitrile solution containing tetramethylammonium tetrafluoroborate as a supporting

electrolyte (0.05 M) using a platinum disk working electrode ( $\phi = 1.6$  mm), a glassy carbon counter-electrode, and Ag/AgCl reference electrode. The concentration of substrates in the working solution was 0.50 mM and the electrochemical potential sweep rate was fixed at 100 mV/s.

The electrochemical properties of the copolymers were investigated by cyclic voltammetry as thin films in deoxygenated anhydrous acetonitrile under nitrogen at a scan rate of 100 mV/s using 0.1 M (n-Bu)<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> as the supporting electrolyte. Pt electrodes were used as both the working and counter electrodes, with Ag/Ag<sup>+</sup> (sat. NaCl) as the pseudoreference electrode. Copolymer films were drop-cast onto the Pt working electrode from a 5 mg/mL CHCl<sub>3</sub> solution. A ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple was used as internal standard and was assigned an absolute energy level of -4.80 eV vs vacuum.

## 1.2 <sup>1</sup>H and <sup>13</sup>C NMR Spectroscopy

400 MHz Bruker Nanobay AVIIIHD and 600 MHz Varian VNMRS spectrometers were used to record <sup>1</sup>H and <sup>13</sup>C spectra of compounds in the indicated deuterated solvent. All chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to residual solvent peaks as follows: CDCl<sub>3</sub> ( $\delta_{\text{H}} = 7.26$  ppm,  $\delta_{\text{C}} = 77.0$  ppm), CD<sub>3</sub>CN ( $\delta_{\text{H}} = 1.94$  ppm,  $\delta_{\text{C}} = 118.3$  ppm). Coupling constants ( $J$ ) are averaged. The multiplicity of <sup>1</sup>H NMR signals is designated by one of the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. The <sup>13</sup>C NMR spectra are <sup>1</sup>H decoupled.



**Figure S1.**  $^1\text{H}$  NMR of **3** in  $\text{CD}_3\text{CN}$ .

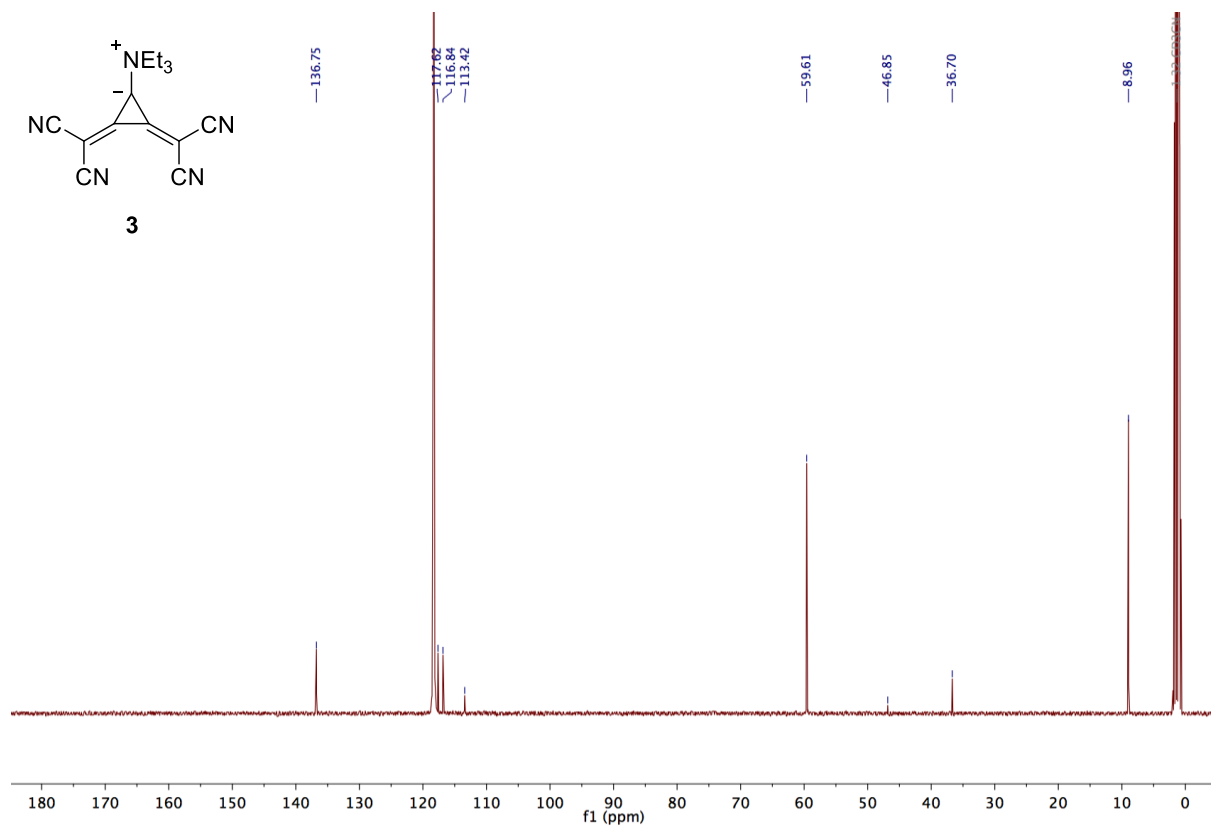
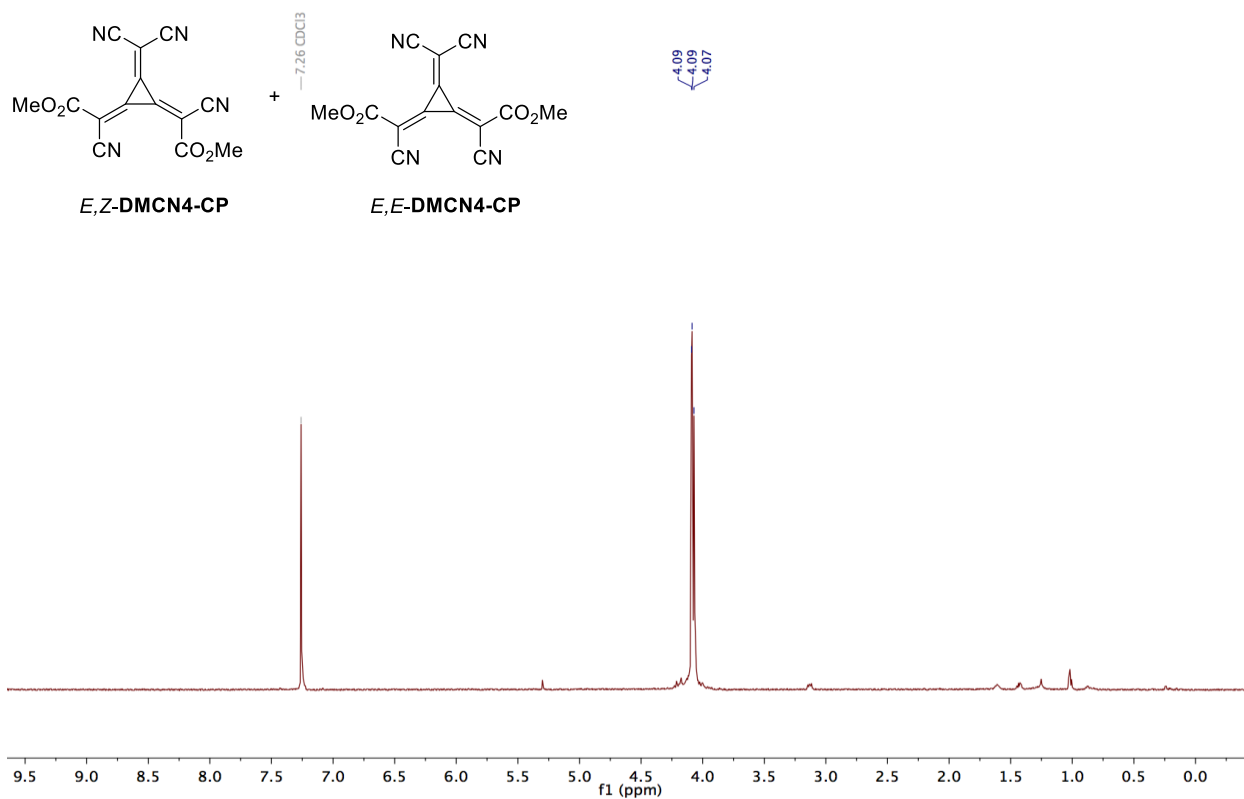
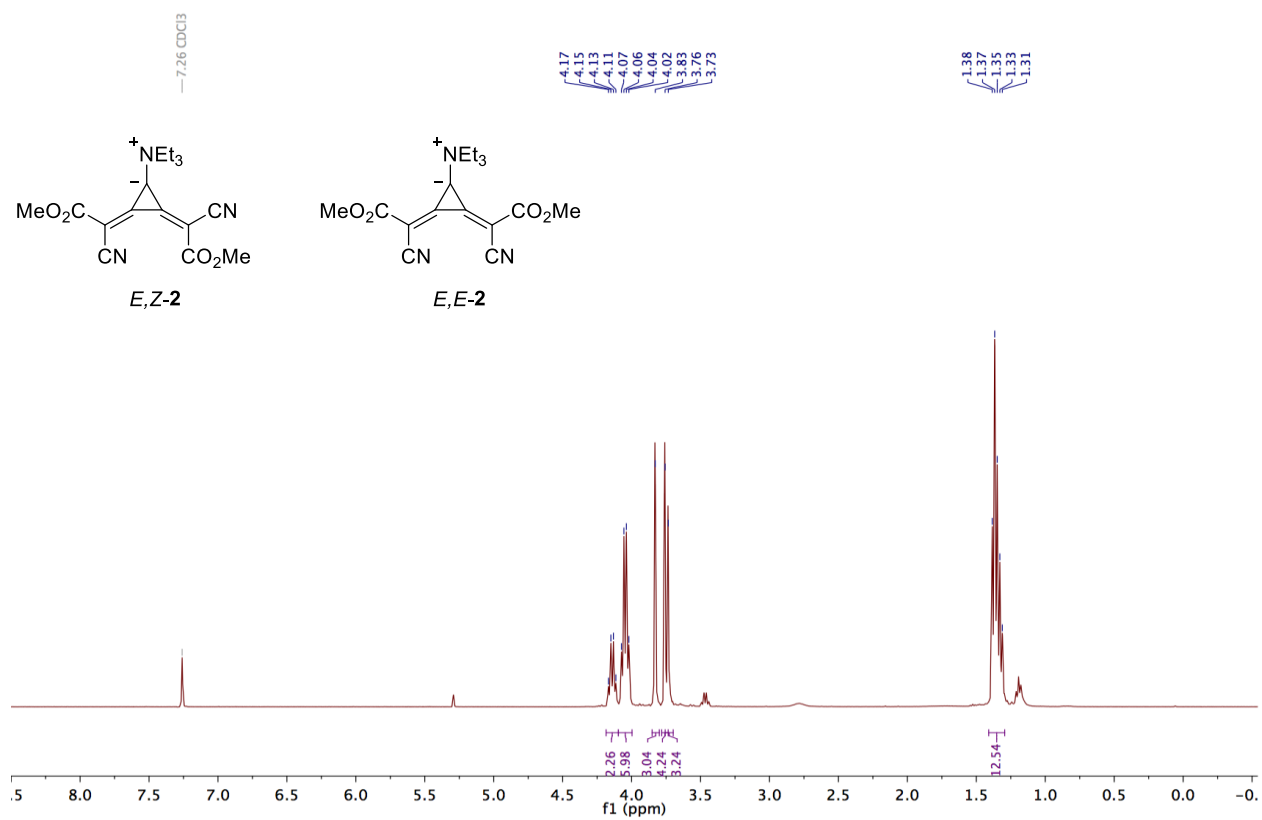


Figure S2. <sup>13</sup>C NMR of **3** in CD<sub>3</sub>CN.



**Figure S3.** <sup>1</sup>H NMR of DMCN4-CP isomer mixture in CDCl<sub>3</sub>.



**Figure S4.** <sup>1</sup>H NMR of **2** isomer mixture in CDCl<sub>3</sub>.

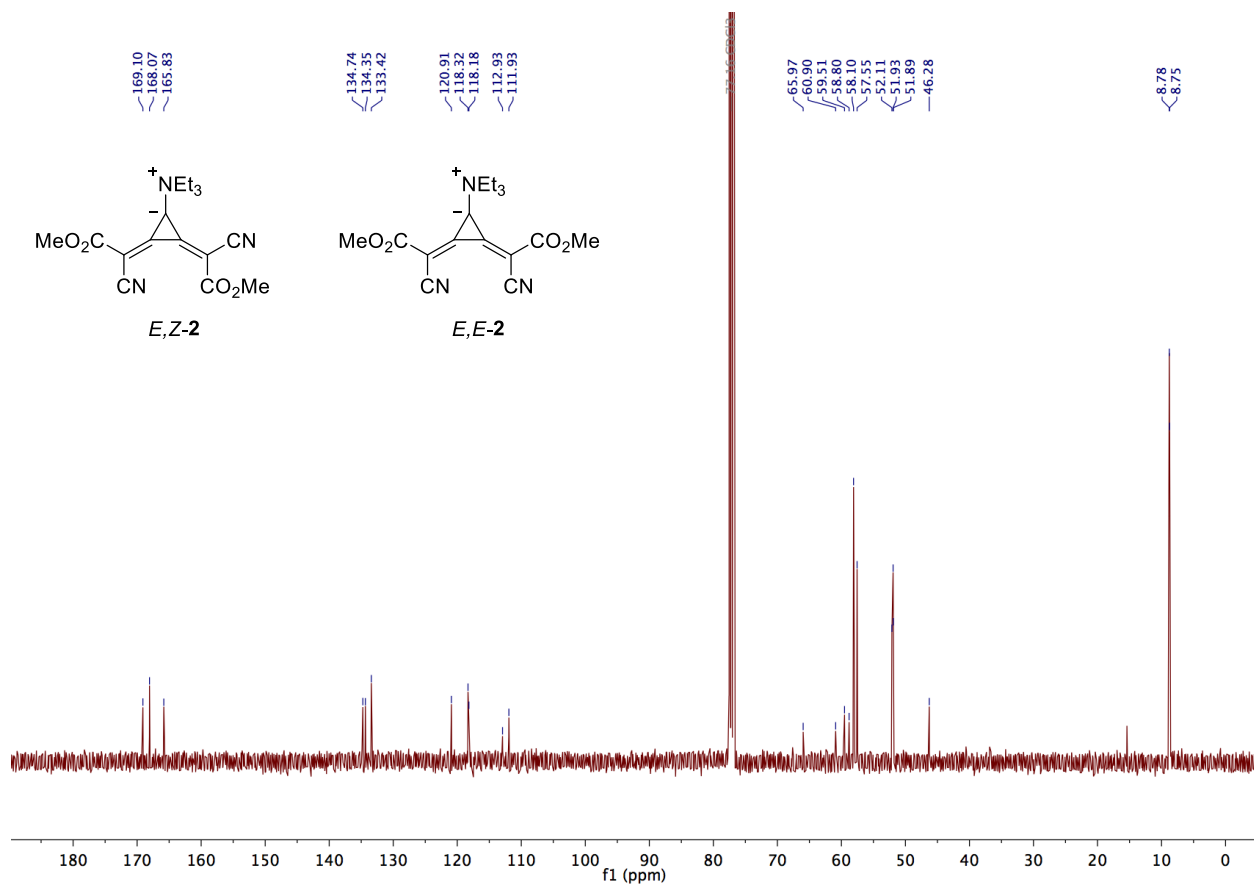


Figure S5.  $^{13}\text{C}$  NMR of **2** isomer mixture in  $\text{CDCl}_3$ .



### 1.3 Dopant Cyclic Voltammetry

Cyclic voltammograms were recorded on a BASi Epsilon MF-9092 electrochemical workstation. Redox potentials were measured in degassed anhydrous acetonitrile solution containing tetramethylammonium tetrafluoroborate as a supporting electrolyte (0.05M) using a platinum disk working electrode ( $\varnothing = 1.6$  mm), a glassy carbon counter-electrode, and Ag/AgCl reference electrode. The concentration of substrates in the working solution was 0.50 mM and the electrochemical potential sweep rate was fixed at 100 mV/s. On the basis of the CV data, the LUMO energy levels were determined from their reduction potentials according to following relationship:  $E_{\text{LUMO}} = -e(E_{\text{red}} + E_{\text{ref}})$ , where  $E_{\text{ref}}$  is 4.72 V for the Ag/AgCl reference electrode used in our measurements.

**Table S1.** Measured reduction potential and calculated LUMO energies for **DMCN4-CP**, **MCN5-CP** and **ECN5-CP**.

<b>Compound</b>	<b><math>E_{\text{red1}}</math> (V)</b>	<b><math>E_{\text{LUMO1}}</math> (eV)</b>	<b><math>E_{\text{red2}}</math> (V)</b>	<b><math>E_{\text{LUMO2}}</math> (eV)</b>
<b>DMCN4-CP</b>	0.89	5.61	0.18	4.90
<b>MCN5-CP<sup>a</sup></b>	1.05	5.77	0.29	5.01
<b>ECN5-CP</b>	1.03	5.75	0.28	5.00

<sup>a</sup> Measured from  $\text{K}^+ \text{MCN5-CP}^{\bullet -}$ .

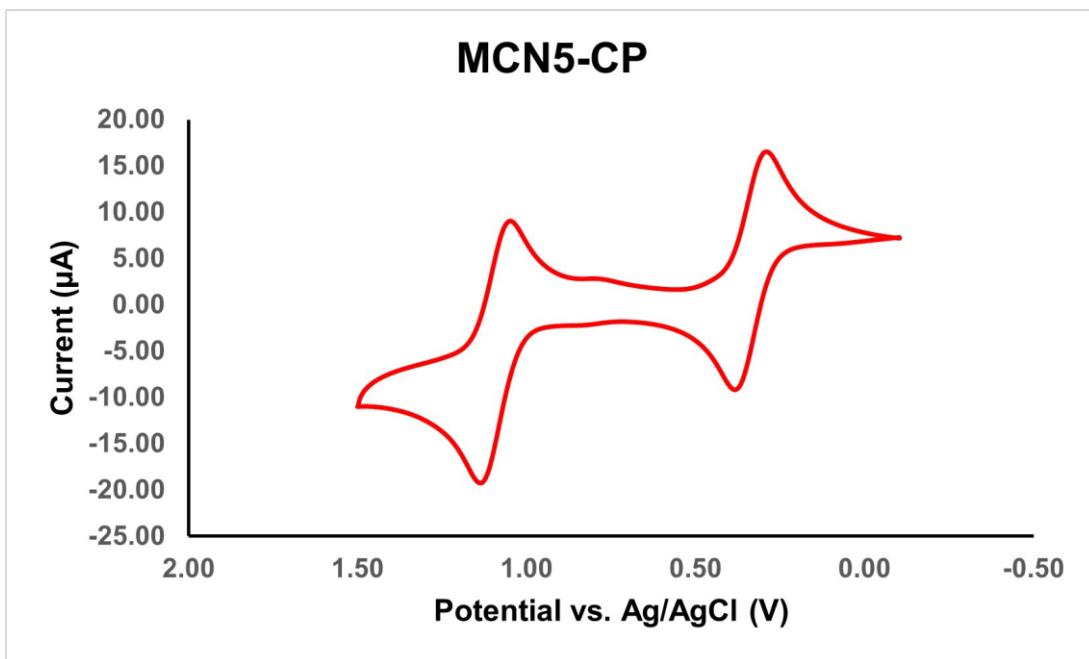


Figure S6. CV trace of MCN5-CP.

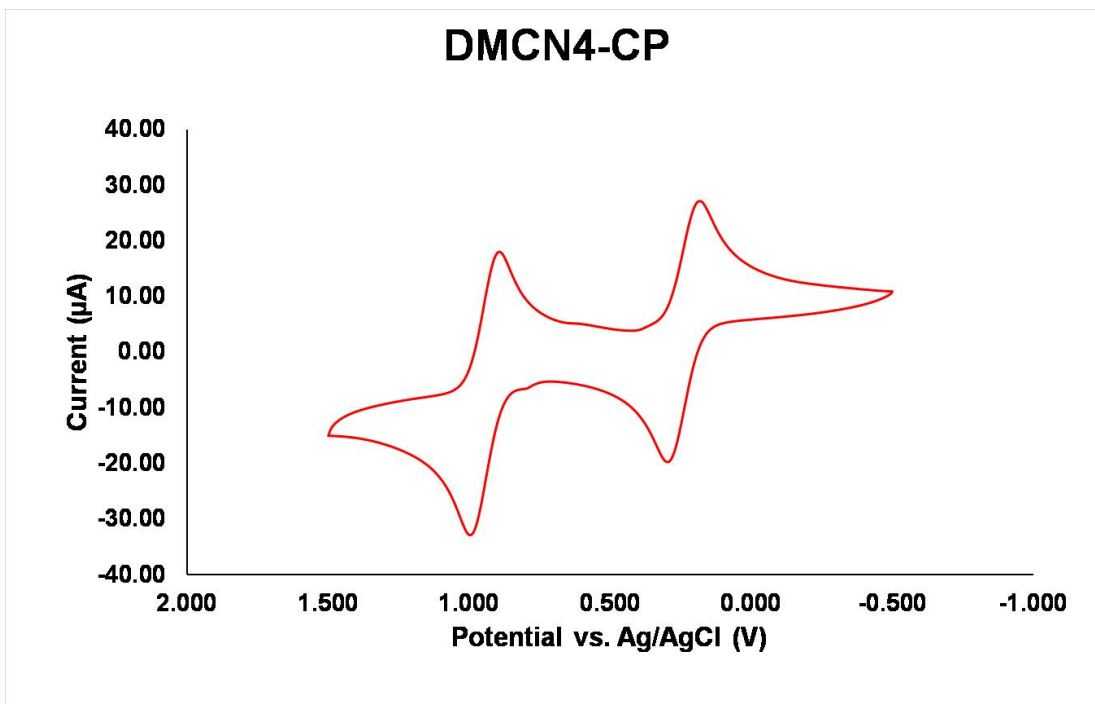


Figure S7. CV trace of DMCN4-CP.

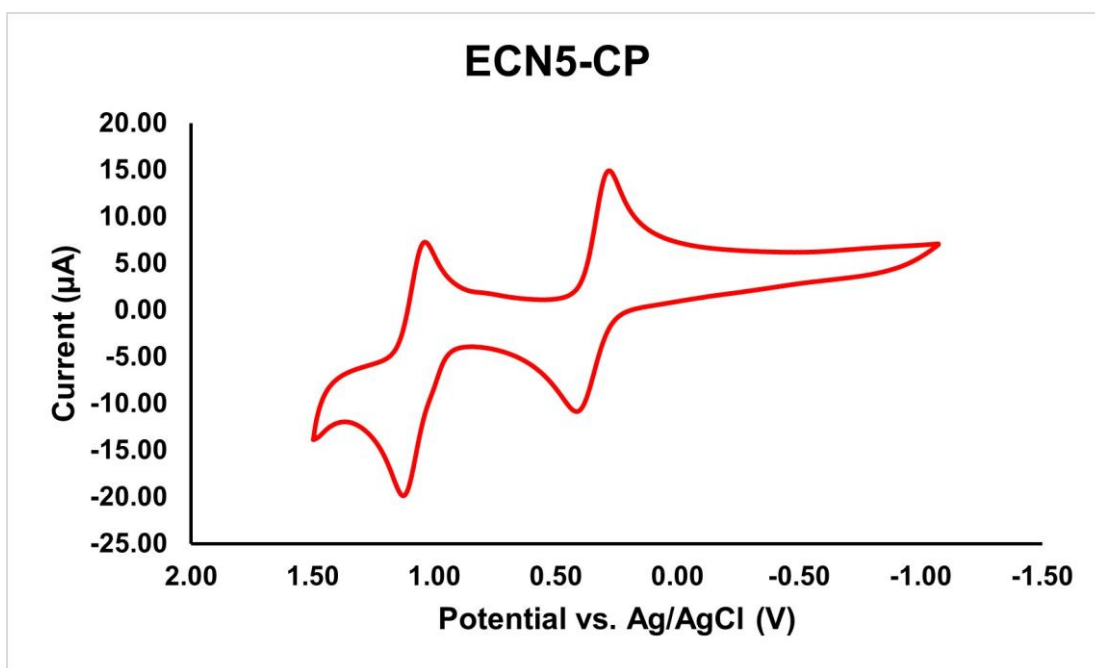


Figure S8. CV trace of ECN5-CP.

## 2 Copolymer Synthesis

### 2.1 Materials and Methods

Precatalyst components  $\text{Pd}_2(\text{dba})_3$  and tri(*o*-tolyl)phosphine were purchased from Sigma-Aldrich and stored in a nitrogen-filled glovebox (< 0.5 ppm  $\text{O}_2$ , < 0.5 ppm  $\text{H}_2\text{O}$ ). Starting DPP monomers 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione<sup>1</sup> and 2,5-bis(2-butyloctyl)-3,6-bis(5-(trimethylstannyl)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione<sup>2</sup> were prepared according to the reported procedures starting from 2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione. The other thiophene-based monomers 2,5-bis(trimethylstannyl)thiophene,<sup>3</sup> 2,2'-bis(trimethylstannyl)-5,5'-bithiophen,<sup>4</sup> and 3,3',4,4'-tetrafluoro-5,5'-bis(tributylstannyl)-2,2'-bithiophene<sup>5</sup> were prepared according to literature procedures. Polymerization solvents DMF and toluene were purchased from Sigma-Aldrich as anhydrous solvents, degassed, and stored in a nitrogen-filled glovebox (< 0.5 ppm  $\text{O}_2$ , < 0.5 ppm  $\text{H}_2\text{O}$ ). All polymerizations were performed under an inert atmosphere with all catalytic components and monomers rigorously purified. Copolymer molecular weights were determined on an Agilent 1260 Infinity II GPC/SEC system equipped with a set of two PLgel 5  $\mu\text{m}$  mixed-C columns using chloroform (stabilized with 250 ppm of ethanol) as the eluent at 50 °C and calibrated with narrow polystyrene standards. Copolymer samples were pre-dissolved at 0.50 mg/mL concentration in chloroform with stirring at 50 °C overnight.

### 2.2 General Procedure

An oven-dried 3 mL Wheaton V-vial equipped with a fitted stir bar was charged with the two comonomers (0.10 mmol each) in a toluene/DMF mixture (5:1, 2.1 mL). A stock catalyst solution was prepared in a separate oven-dried 20 mL scintillation vial by dissolving  $\text{Pd}_2(\text{dba})_3$  (0.01 mmol) and  $\text{P}(\text{o-tol})_3$  (0.04 mmol, 1:2 Pd/ligand molar ratio) in a toluene/DMF mixture (5:1, 1.0 mL). The stock catalysts and comonomer solutions were stirred for 15-30 min until completely homogenous. The necessary quantities of the stock catalyst solution (0.10 mL, providing 2 mol% of the Pd catalyst) were added to the V-vial with co-monomers using a 1 mL gas-tight syringe to give the final concentration of monomers (~0.045 M). The vial was sealed

with a Teflon-lined Mininert pressure screw cap. The reaction mixture was heated at 120 °C (external temperature, internal temperature ~113-114 °C) with stirring for 18 h using a aluminum heating block. Upon completion, the reaction mixture was cooled to RT, 0.025 mL of 2-(tributylstannyl)thiophene was added through the Mininert valve and the reaction was stirred at 120 °C for another 2 h. The mixture was again cooled to RT, 0.05 mL of 2-bromothiophene was added through the Mininert valve, and the reaction was stirred at 120 °C for an additional 2 h. After cooling to room temperature, the polymer was precipitated into 100 mL of methanol containing 1 mL 12 N HCl with vigorous stirring. After 15 min, the polymer was filtered through a cellulose extraction thimble and subjected to Soxhlet extraction using methanol, acetone, hexane, chloroform, in that order. After the final extraction, the polymer solution was concentrated to ca. 10% of the original volume and precipitated into 100 mL of methanol with vigorous stirring. The polymer product was collected by filtration through a nylon membrane and dried overnight under high vacuum (100 mTorr) at 60 °C to give the polymer product.

**Table S2.** Summary of the copolymer data.

<b>Copolymer</b>	<b>Yield (%)</b>	<b><math>M_w</math> (kg/mol)</b>	<b><math>M_n</math> (kg/mol)</b>	<b><math>\bar{D}</math></b>
pDPP-2T	77.5	325.1	64.5	5.04
pDPP-3T	69.4	163.7	43.9	3.73
pDPP-2T-2T4F4	72.0	137.2	25.5	5.38

### 2.3 VT <sup>1</sup>H NMR Spectroscopy of Polymers

High Temperature NMR spectra of the copolymers were recorded at 120 °C on a Bruker Avance 500 DRX Spectrometer (FT, 500 MHz) temperature-calibrated with ethylene glycol standards. All copolymer samples were prepared at a concentration of 1.5 mg/mL in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>. Chemical shifts for <sup>1</sup>H spectra are referenced to the residual <sup>1</sup>H-NMR signal ( $\delta$  6.00 for C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>). Chemical shifts are in ppm.

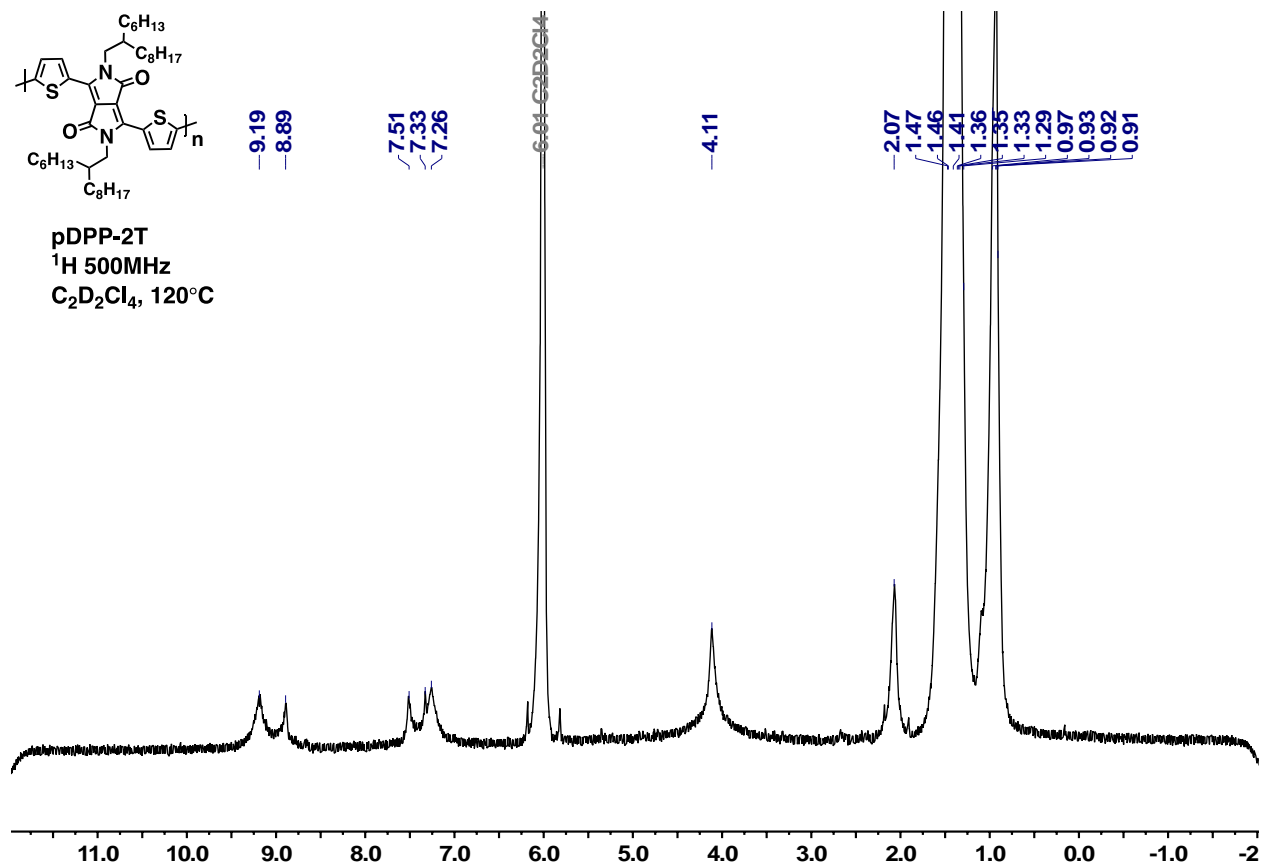


Figure S9. <sup>1</sup>H NMR of pDPP-2T in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 120 °C.

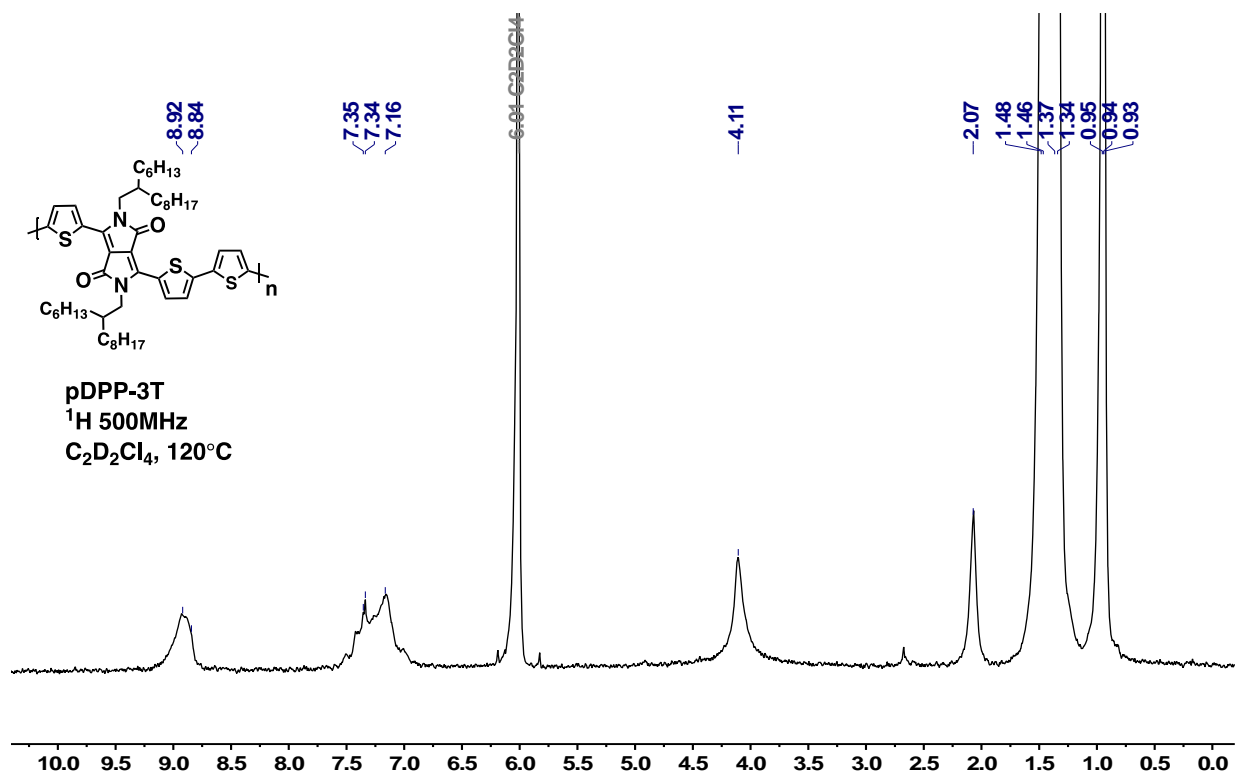
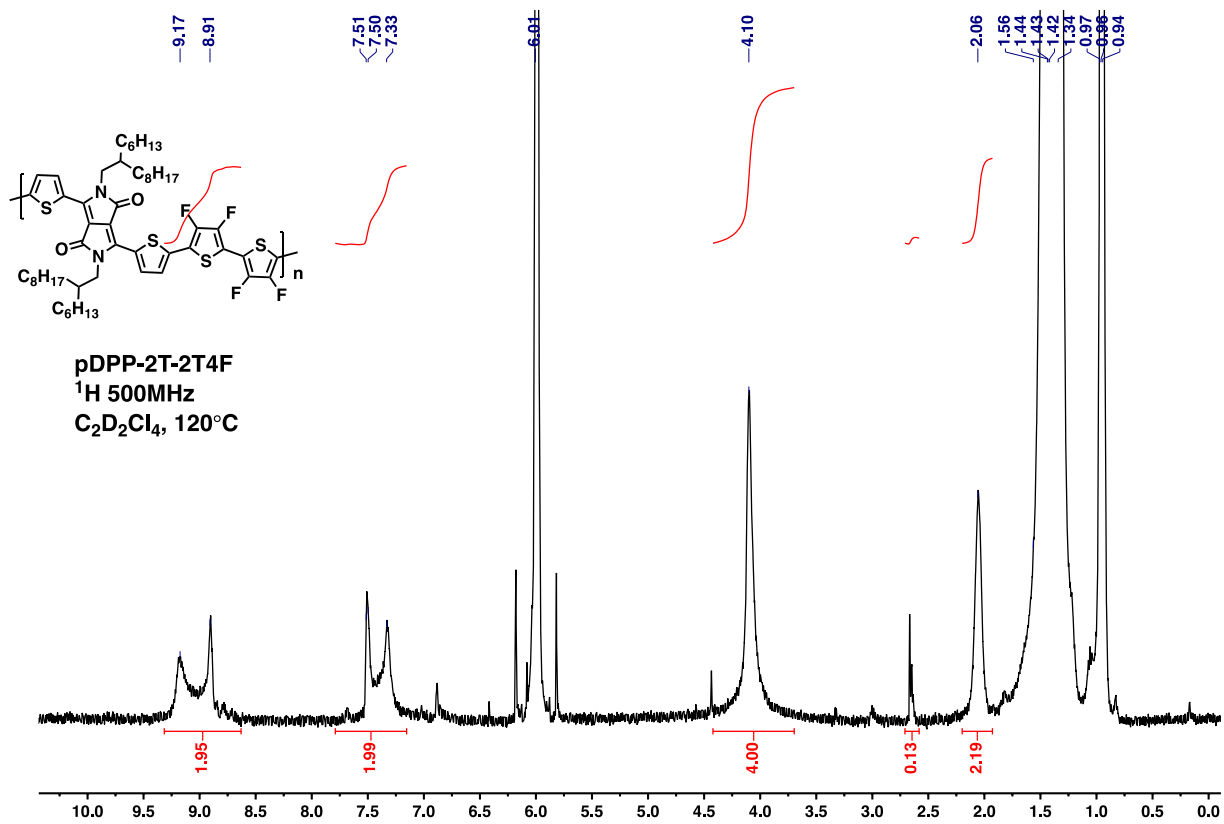


Figure S10.  $^1\text{H}$  NMR of pDPP-3T in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 120 °C.



**Figure S11.** <sup>1</sup>H NMR of pDPP-2T-2T4F in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 120 °C.



## 2.4 Polymer Cyclic Voltammetry

The electrochemical properties of the copolymers were investigated as thin films in deoxygenated anhydrous acetonitrile under nitrogen at a scan rate of 100 mV/s using 0.1 M tetrakis(*n*-butyl)ammonium hexafluorophosphate [(*n*-Bu)<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup>] as the supporting electrolyte. Pt electrodes were used as both the working and counter electrodes, with Ag/AgCl (sat. NaCl) as the pseudoreference electrode. Copolymer films were drop-cast onto the Pt working electrode from a 5 mg/mL CHCl<sub>3</sub> solution. A ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple was used as the internal standard and assigned an absolute energy level of -4.80 eV vs vacuum. The HOMO energies of the copolymers were determined according to the equation  $E_{\text{HOMO}} = (E_{\text{ox}}^{\text{onset}} + 4.80)$ , where  $E_{\text{ox}}^{\text{onset}}$  is the onset of oxidation relative to the measured Fc/Fc<sup>+</sup> redox couple. The Fc/Fc<sup>+</sup> redox couple was found at 0.45 V relative to the Ag/Ag<sup>+</sup> electrode.

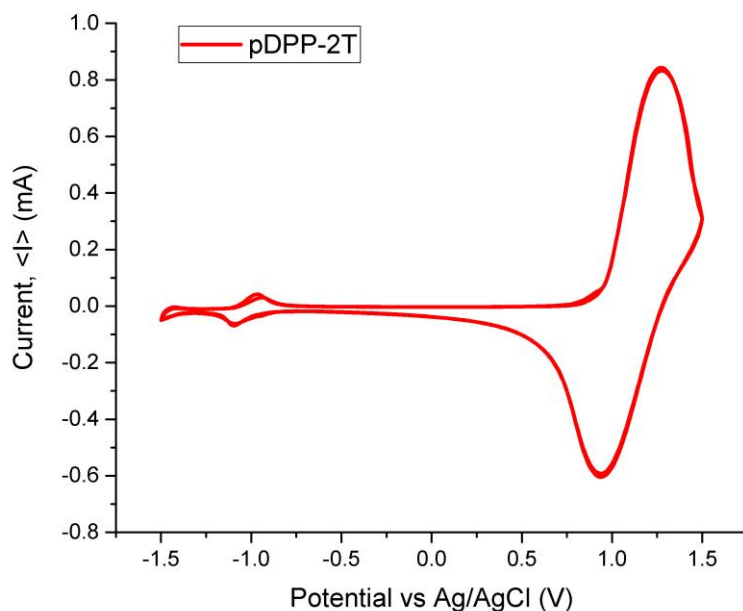
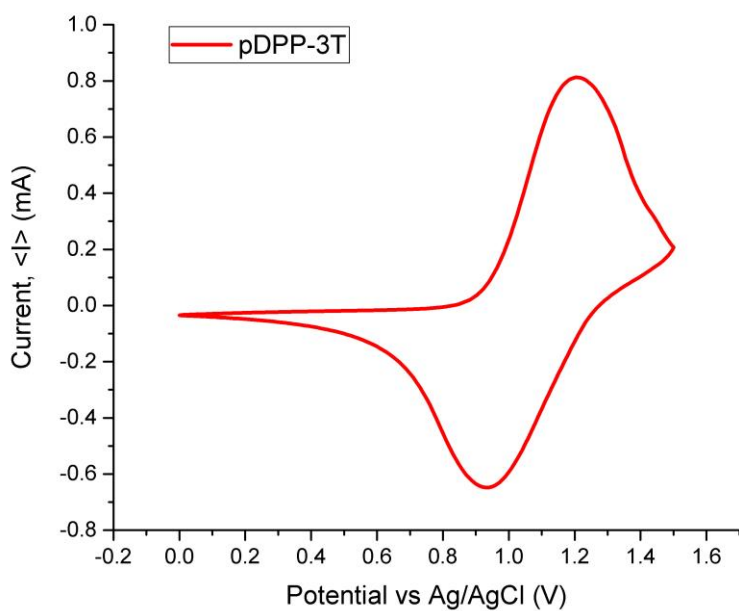
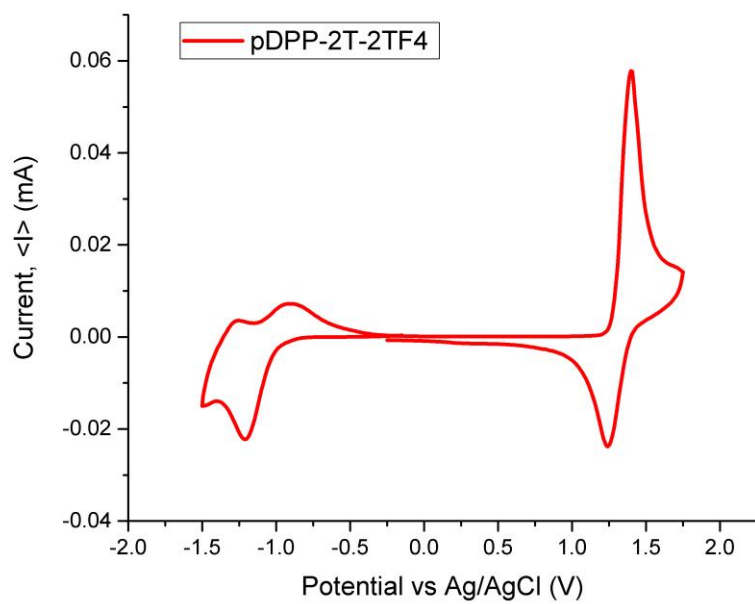


Figure S12. CV trace of pDPP-2T.



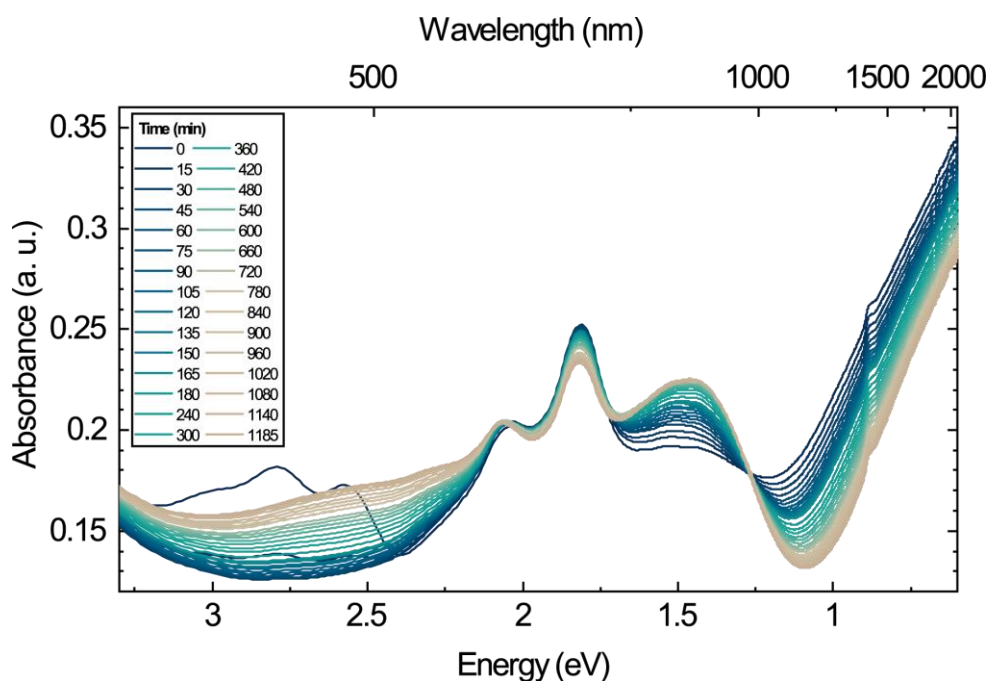
**Figure S13.** CV trace of pDPP-3T.



**Figure S14.** CV trace of pDPP-2T-2TF4.

### 3 Dopant Stability Measurements

In order to determine the stability of doped films, a lifetime analysis was performed using the UV-vis-NIR data. Two sets of samples P3HT samples doped with 1.0 mg/ml of ECN5-CP were fabricated and then stored either in air or in N<sub>2</sub> glove box (both sets of samples were covered and kept dark). The samples were measured periodically using the UV-vis-NIR to determine whether the polaron density is reduced. We do not have the ability to measure UV-vis-NIR in N<sub>2</sub>, so samples stored under N<sub>2</sub> were taken into and out of the glovebox anti-chamber between measurements.

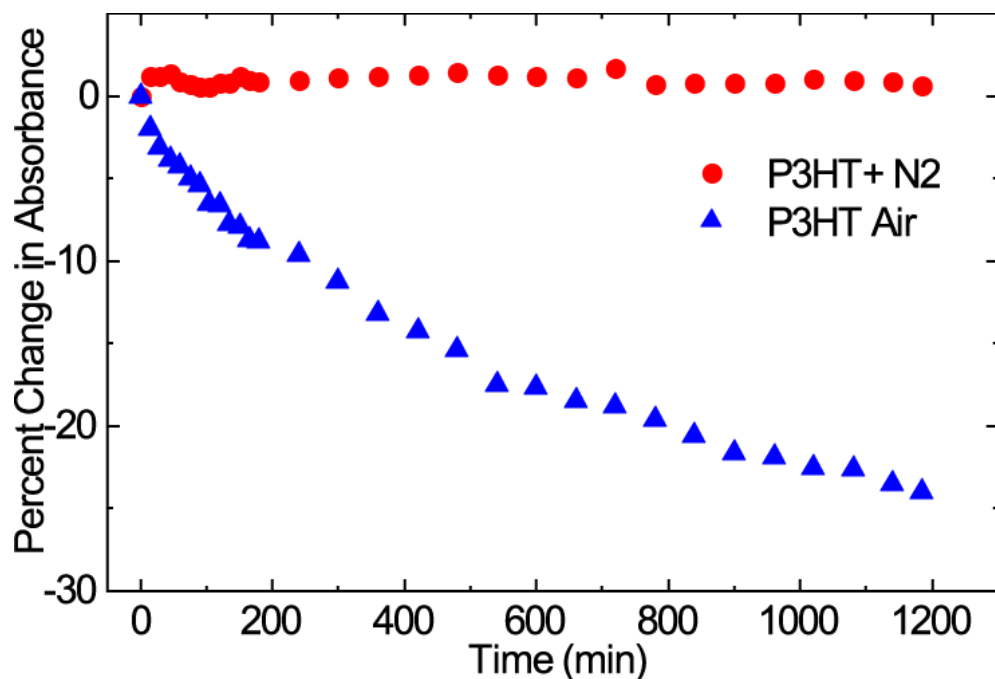


**Figure S15.** UV-vis-NIR of P3HT sequentially doped with 1.0 mg/mL ECN5-CP. The spectra were acquired as a function of time. The UV/vis measurements were in air, but the sample was stored in N<sub>2</sub> between measurements.

Figure S15 shows the UV/vis/NIR spectra taken as a function of time. The polaron peaks clearly bleach with time while the neutral absorbance increases. The features at 2.5-3 eV are neutral dopant, which is gone within <1 min. Note that we attempted to isolate the neutral dopant for UV-vis-NIR characterization, but were unable to measure a pure signal because the sample had already partially reduced in air prior to measurement. The lifetime result shows the high

propensity of the neutral dopants to react with trace contaminants from the air. The ionized dopant is much more robust. The two peaks at 1.8 and 2.0 eV are dopant anion. These peaks are robust to exposure to air.

Figure S16 shows the percentage change in absorbance for the polaron in a P3HT/**ECN5-CP** sample that was held in air vs stored under N<sub>2</sub>. The polaron signal was monitored using the UV/vis signal at 2000 nm, which corresponds to polaron absorbance only. The result clearly shows a reduction in polaron density and therefore doping for the sample stored in air while the sample stored under N<sub>2</sub> does not show significant change in absorbance.



**Figure S16.** Comparison of P3HT/**ECN5-CP** stored in air vs stored in an N<sub>2</sub> glovebox.

#### 4 Additional references

1. Mueller, C. J.; Gann, E.; McNeill, C. R.; Thelakkata, M. *J. Mater. Chem. C*, **2015**, *3*, 8916.
2. Wang, J. L.; Chang, Z.F.; Song, X. X.; Liu, K. K.; Ling-Min Jing, L. M.; *J. Mater. Chem. C*, **2015**, *3*, 9849.
3. Lee, J.; Kim, J. W.; Park, S. A.; Son, S. Y., Choi, K.; Lee, W. *Advanced Energy Materials*, **2019**, *9*, 1901829.
4. Watanabe, K.; Osaka, I., Yorozyu, S.; Akagi, K. *Chemistry of Materials*, **2012**, *24*, 1011.
5. Kawashima, K.; Fukuhara, T.; Suda, Y.; Suzuki, Y.; Koganezawa, T.; Yoshida, H.; Ohkita, H.; Osaka, I.; Takimiya, K. *J. Am. Chem. Soc.* **2016**, *138*, 10265.