

# Supporting Information for: Protonic Acid Doping of Low Band-gap Conjugated Polyions

Gang Ye<sup>1,2</sup>, Yuru Liu<sup>1,2</sup>, Jian Liu<sup>2</sup>, Xinkai Qiu<sup>1,2</sup>, L. Jan Anton Koster<sup>2</sup> and Ryan C. Chiechi<sup>\*1,2</sup>

<sup>1</sup>*Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands*

<sup>2</sup>*Zernike Institute for Advanced Materials, Nijenborgh 4, 9747 AG Groningen, the Netherlands*

*\*e-mail: r.c.chiechi@rug.nl*

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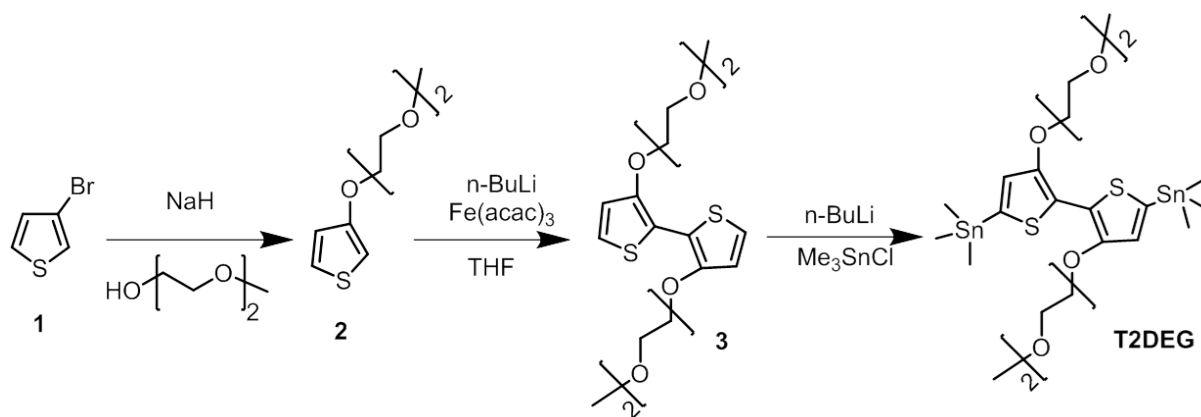
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# 1 Synthesis

## General

All reagents and solvents were commercial and were used without further purification unless otherwise indicated. Monomer 1 and monomer 2 were synthesized according to literature procedures.<sup>1-5</sup>

**Measurement and characterization.** <sup>1</sup>H NMR and <sup>13</sup>C NMR were performed on a Varian Unity Plus (400 MHz) instrument at 25 °C, using tetramethylsilane (TMS) as an internal standard. NMR shifts are reported in ppm, relative to the residual protonated solvent signals of CDCl<sub>3</sub> ( $\delta = 7.26$  ppm) or DMSO-d<sub>6</sub> ( $\delta = 2.50$  ppm) and at the carbon absorption in CDCl<sub>3</sub> ( $\delta = 77.23$  ppm) or DMSO-d<sub>6</sub> ( $\delta = 39.52$  ppm). Multiplicities are denoted as: singlet (s), doublet (d), triplet (t) and multiplet (m). FT-IR spectra were recorded on a Nicolet Nexus FT-IR fitted with a Thermo Scientific Smart iTR sampler. EPR spectra were recorded on a Magnettech MiniScope MS400 using a quartz capillary at a concentration of 0.5-1 mg mL<sup>-1</sup> in HCOOH or CF<sub>3</sub>COOH. UV-vis-NIR measurements were carried out on a Shimadzu UV 3600 spectrometer in 1 cm fused quartz cuvettes with concentrations of 0.01 mg mL<sup>-1</sup>. Cyclic voltammetry (CV) was carried out with a Autolab PGSTAT100 potentiostat in a three-electrode configuration where the working electrode was a glassy carbon, the counter electrode was a platinum wire, and the pseudo-reference was an Ag wire that was calibrated against ferrocene (Fc/Fc<sup>+</sup>).



**Figure S1:** Synthetic route for **Monomer T2DEG**.

## Monomers

### 3-(2-(2-methoxyethoxy)ethoxy)thiophene 2

In a dry three-neck round-bottom flask, 60 % NaH (1200 mg, 30 mmol) was mixed with anhydrous DMF (20 mL) under a nitrogen atmosphere. Triethylene glycol monomethyl ether (12 g, 11.68 mL, 100 mmol) was added drop-wise over a period of 30 minutes at 0 °C. The solution was allowed to stir for additional one hour. To this reaction mixture, 3-bromothiophene (3.2 g, 1.84 mL, 20 mmol) and CuBr (280 mg, 2 mmol) were added. The ice bath was replaced with an oil bath and the solution was heated up to 110 °C for another one hour. After cooling to the room temperature, the mixture was then poured into NH<sub>4</sub>Cl aqueous solution and stirred for 10 minutes. The organic phase was extracted with *n*-hexane, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Then, the solvent was evaporated by rotary evaporation. The crude solid was purified by column chromatography (silica gel) by using ethyl acetate:hexane (1:2) as eluent to give pure target product 2 (3.6 g, 90 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ: 7.15 (dd, <sup>3</sup>J<sub>H,H</sub> = 5.3 Hz, <sup>4</sup>J<sub>H,H</sub> = 3.2 Hz, 1H), 6.76 (dd, <sup>3</sup>J<sub>H,H</sub> = 5.3 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.5

Hz, 1H), 6.24 (dd,  $^4J_{H,H} = 3.2$  Hz,  $^4J_{H,H} = 1.5$  Hz, 1H), 4.11 (t,  $^3J_{H,H} = 4.8$  Hz, 2H), 3.83 (t,  $^3J_{H,H} = 4.8$  Hz, 2H), 3.69 (t,  $^3J_{H,H} = 4.8$  Hz, 2H), 3.56 (t,  $^3J_{H,H} = 4.8$  Hz, 2H), 3.37 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 157.4, 124.5, 119.4, 97.3, 71.8, 70.5, 69.5, 69.4, 58.9.

### **3,3'-bis(2-(2-methoxyethoxy)ethoxy)-2,2'-bithiophene 3**

To a solution of 3-(2-methoxyethoxy)thiophene 2 (1.8 g, 8.91 mmol) in anhydrous THF (20 mL) at ice bath, the *n*-BuLi (8.91 mmol, 5.57 mL, 1.6M in Hexane) were added dropwise over 10 min at 0 °C under  $\text{N}_2$  condition. The mixture was kept stirring at this temperature for 2 hours before the solution was transferred to another dry flask with  $\text{Fe}(\text{acac})_3$  (3.15 g, 9.8 mmol) in THF (70 mL), the reaction mixture was then heated under reflux for 3 hours. After cooling to room temperature, the precipitate was filtered off through short silica plug eluting with 5 %  $\text{CH}_3\text{OH}$  in  $\text{CH}_2\text{Cl}_2$ . The filtrate was washed with saturated  $\text{NH}_4\text{Cl}$  solution and the aqueous phases were combined and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic phases were dried over  $\text{Na}_2\text{SO}_4$  and the solvent was evaporated by rotary evaporation. The crude solid was purified by column chromatography (silica gel) by using ethyl acetate:hexane (1:1) as eluent to give target product **3** with a little red color impurities. The crude product was then purified by recrystallization in  $\text{Et}_2\text{O}$  to give pure product **3** (900 mg, 50 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 7.05 (d,  $^3J_{H,H} = 5.2$  Hz, 2H), 6.83 (d,  $^3J_{H,H} = 5.2$  Hz, 2H), 4.24 (t,  $^3J_{H,H} = 4.8$  Hz, 4H), 3.89 (m, 4H), 3.72 (m, 4H), 3.55 (m, 4H), 3.37 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 144.0, 121.9, 116.5, 114.7, 72.0, 71.4, 70.8, 70.0, 59.1.

### **Monomer T2DEG**

(3,3'-bis(2-(2-methoxyethoxy)ethoxy)-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane)

Compound 3,3'-bis(2-methoxyethoxy)-2,2'-bithiophene 3 (402 mg, 1 mmol) was dissolved in anhydrous THF (10 mL) under an atmosphere of N<sub>2</sub>, cooled to -78 °C and n-butyllithium (2.15 mmol, 1.35 mL, 1.6 M in hexane) was added dropwise. The solution was stirred for 2 hours in the cold bath at -78 °C before being warmed to room temperature and stirred for an additional 15 minutes. The mixture was cooled to -78 °C again. Then, trimethyltin chloride (3 mL, 3 mmol, 1.0 M in THF) was added. After that, the solution was stirred at room temperature overnight. Water was added to quench the reaction, and the solution was extracted with *n*-hexane. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed by rotary evaporation leading to the crude compound as an yellow oil which was purified by recrystallization in isopropanol. The pure monomer **T2DEG** (518 mg) was obtained in 71 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ: 6.90 (s, 1H), 4.28 (t, <sup>3</sup>J<sub>H,H</sub> = 4.8 Hz, 2H), 3.92 (t, <sup>3</sup>J<sub>H,H</sub> = 4.8 Hz, 2H), 3.76 (t, <sup>3</sup>J<sub>H,H</sub> = 4.8 Hz, 2H), 3.57 (t, <sup>3</sup>J<sub>H,H</sub> = 4.8 Hz, 2H), 3.39 (s, 3H), 0.36 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ: 153.8, 134.1, 124.4, 120.9, 72.3, 71.7, 71.1, 70.4, 59.3, -8.1.

## Polymers

### General synthetic procedures for polymers

To a dry three-neck flask, Monomer 1 (1 eq), Monomer 2 (2 eq) and Distannyl derivatives (3 eq) were added under N<sub>2</sub> followed by Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>)

(10 %mol). The flask and its contents were subjected to 3 pump/purge cycles with N<sub>2</sub> followed by addition of anhydrous oxygen-free DMF (5 mL) via syringe. The reaction mixture was vigorously stirred at 110 °C for three days. After cooling to room temperature, the reaction mixture was poured into 200 mL vigorously stirred acetone. The precipitated solid was collected by filtration. The solid polymers were suspended in milipore water, and transferred into a dialysis tube (MWCO:3500). The dialysis tube was placed into a large beaker with water (2 L) stirring for 3 days, and the water was changed every 12 hours. After the dialysis, the solid was collected and dried under vacuum overnight.

CPIZ-T: Synthesis according to the general polymerization procedure: monomer 1 (44 mg, 0.1 mmol), monomer 2 (92 mg, 0.2 mmol) and 2,5-bis(trimethylstannyl)thiophene (123 mg, 0.3 mmol). The polymers were obtained as a yellow solid (81 mg, 72 %). <sup>1</sup>H NMR (400 MHz, TFA-d): δ: 8.4–6.7 (m, Ar-H, 36H), 4.5–2.7 (m, N-CH<sub>3</sub> + CH<sub>2</sub>, 16H). IR (cm<sup>-1</sup>): 695, 741, 759, 798, 905, 946, 973, 1016, 1153, 1187, 1350, 1405, 1443, 1495, 1518, 1563, 1607, 3356.

CPIZ-TT: Synthesis according to the general polymerization procedure: monomer 1 (22 mg, 0.05 mmol), monomer 2 (46 mg, 0.1 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (74 mg, 0.15 mmol). The polymers were obtained as a yellow-orange solid (60 mg, 87 %). <sup>1</sup>H NMR (400 MHz, TFA-d): δ: 8.83–7.71 (m, Ar-H, 42H), 4.88–3.50 (m, N-CH<sub>3</sub> + CH<sub>2</sub>, 16H). IR (cm<sup>-1</sup>): 668, 689, 741, 794, 854, 927, 948, 1064, 1107, 1196, 1348, 1394, 1440, 1519, 1563, 1599, 2917, 3384.

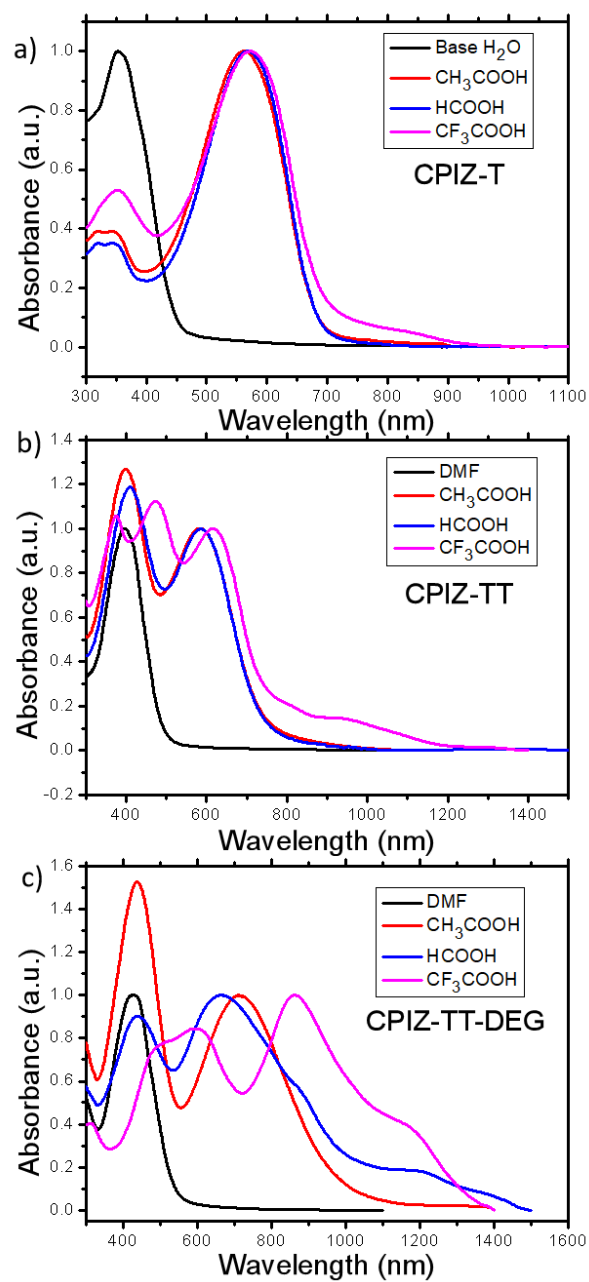
CPIZ-TT-DEG: Synthesis according to the general polymerization procedure: monomer 1 (22 mg, 0.05 mmol), monomer 2 (46 mg, 0.1 mmol) and T2DEG (110 mg, 0.15 mmol). The polymers were

obtained as a orange solid (60 mg, 58 %)  $^1\text{H}$  NMR (400 MHz, TFA-d):  $\delta$ : 8.88–6.88 (m, Ar-H, 36H), 5.29–3.54 (m, N-CH<sub>3</sub> + -CH<sub>2</sub>-+O-CH<sub>3</sub>, 82H). IR (cm<sup>-1</sup>): 691, 741, 813, 927, 1066, 1105, 1197, 1348, 1387, 1436, 1503, 1520, 1567, 1601, 2895, 3395.

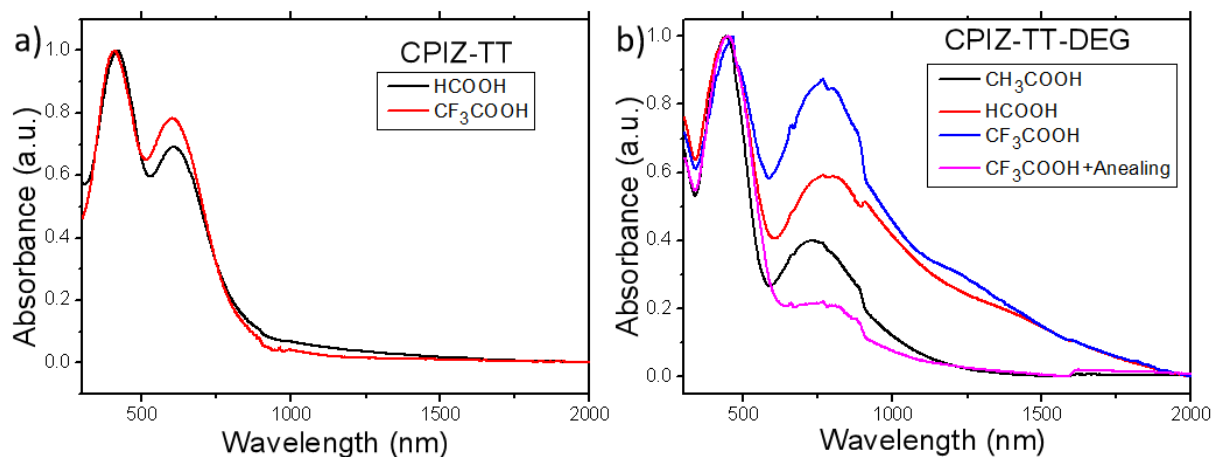


## **2 Characterization**

### **Solution absorption**



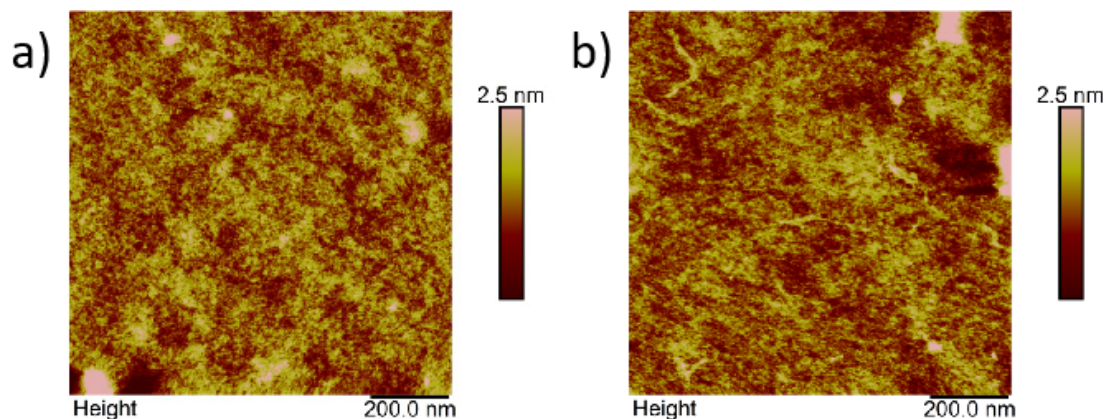
**Figure S2:** a) Absorption spectra of **CPIZ-T** in basic or different acidic solutions ( $10^{-5}\text{M}$ ). b) Absorption spectra of **CPIZ-TT** in basic or different acidic solutions ( $10^{-5}\text{M}$ ). c) Absorption spectra of **CPIZ-TT-DEG** in basic or different acidic solutions ( $10^{-5}\text{M}$ ).



**Figure S3:** a) Absorption spectra of thin films of the **CPIZ-TT** cast from different acidic solutions. b) Absorption spectra of thin films of the **CPIZ-TT-DEG** cast from different acidic solutions.

### Thin film absorption

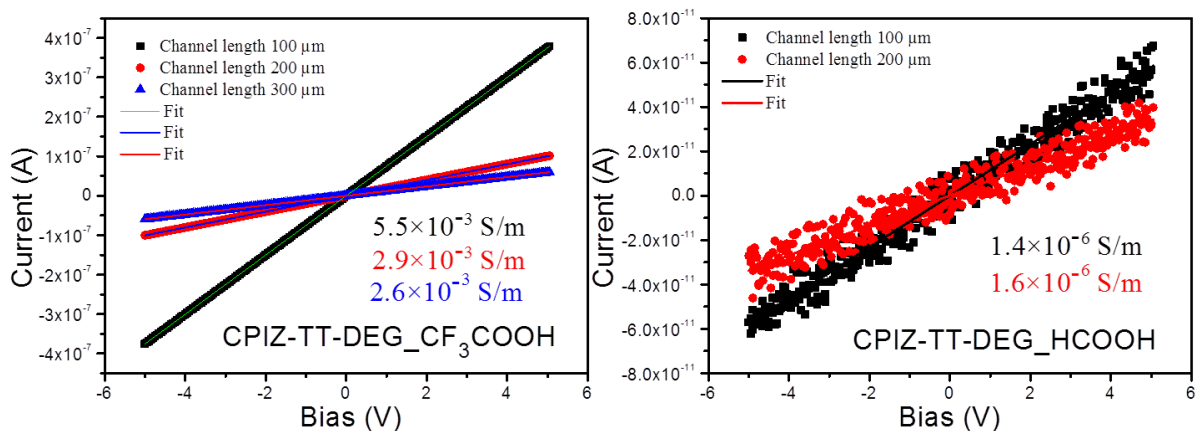
We prepared CPIs thin film for absorption measurements by drop cast from difference acidic solutions (**CPIZ-TT** in  $5 \text{ mg mL}^{-1}$  HCOOH or  $\text{CF}_3\text{COOH}$  and **CPIZ-TT-DEG** in  $10 \text{ mg mL}^{-1}$  HCOOH or  $\text{CF}_3\text{COOH}$ ) on glass. The measurements were carried out on a Shimadzu UV 3600 spectrometer.



**Figure S4:** Surface topographic AFM image of **CPIZ-TT-DEG** spun cast from a) HCOOH and b)  $\text{CF}_3\text{COOH}$  on bare glass surface ( $25 \mu\text{m}^2$ ). The RMS values are 0.56 nm and 2.44 nm for cast from a) HCOOH and b)  $\text{CF}_3\text{COOH}$

### Film Morphology

The characterization of the surface morphology was performed on a Bruker AFM multimode MMAFM-2 equipped with a PeakForce TUNA application module (Brüker). PeakForce tapping AFM was performed with a ScanAsyst-Air probe (resonant frequency 70 kHz, spring constant  $0.4 \text{ N m}^{-1}$ , Brüker) at a scan rate of 0.8 Hz and 800 samples per line. The data were analyzed with Nanoscope Analysis 1.5 (provided by Brüker).



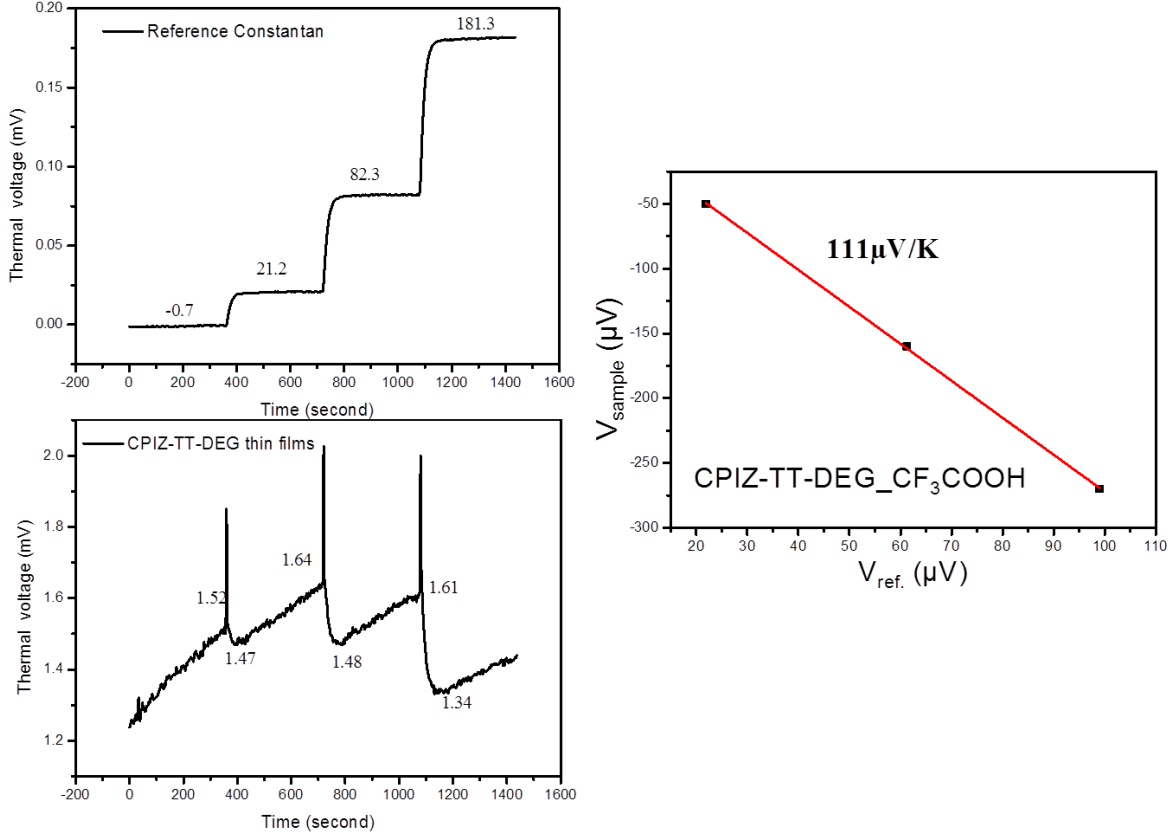
**Figure S5:** a) Channel length dependence of **CPIZ-TT-DEG** conductivity cast from CF<sub>3</sub>COOH. b) Channel length dependence of **CPIZ-TT-DEG** conductivity cast from HCOOH.

## Measurement of electrical conductivity

For the electrical conductivity measurements of the CPIs polymers, parallel line-shape Au electrodes with a width ( $w$ ) of 13 mm and a channel length ( $L$ ) of 100  $\mu\text{m}$  to 300  $\mu\text{m}$  were deposited as the bottom contact before spin-coating. Voltage-sourced two-point conductivity measurements were conducted with a probe station in a N<sub>2</sub> glovebox. The electrical conductivity ( $\sigma$ ) was calculated according to the formula:  $\sigma = (J/V) \times L / (w \times d)$ .

## Seebeck coefficient measurement

The Seebeck coefficient of **CPIZ-TT-DEG** polymers thin-film samples were measured in a home-built setup reported previously.<sup>6-8</sup> Two pairs of Au line electrodes (width: 1 mm and length: 7 mm; width: 1 mm and length: 4 mm) were deposited on a glass substrate with a distance of 7 mm. A thin film was spin-cast on the area (7 mm × 7 mm) defined by the two longer Au electrodes (the part of the substrate beyond that area was covered by scotch tape before coating). A standard constantan wire (with a diameter of 127  $\mu\text{m}$  from Omega) was attached on the other Au line electrodes (width: 1 mm and length: 4 mm) with silver paste (ELECTRODAG 1415). The temperature difference across the sample was set by a thin film heater (KFR-5-120-C1-16, KYOWA), which was attached on top of a small copper block (3mm×14mm×2mm) that sits in front of the active area parallel to the Au lines. The heater was controlled by Keithley 2635. The generated thermal voltages from constantan wire (reference,  $V_{ref}$ ) and thin-film sample ( $V_{sample}$ ) were probed by four probes at the same time and corresponding data were recorded by Keithley 2000 with a scanning card. A step-by-step increased temperature method was used and a home-made filter (cut-off frequency = 1 Hz) was used for reducing the noise. The substrate temperature was obtained by a T-type thermocouple (Omega, the cold junction was connected on the chamber, whose temperature was detected by Pt100 sensor). The system is controlled by Labview software. The Seebeck coefficient (S) of sample was obtained by the formula:



**Figure S6:** Time evolution of the thermal voltage of the reference constantan wire (the black symbols) and **CPIZ-TT-DEG** thin films cast from the  $CF_3COOH$ . The corresponding plots of thermal  $V_{sample}$  versus thermal  $V_{ref}$  with the linear fits.

$$S = \frac{V_{sample}}{V_{ref}} S_{const} + \left( \frac{V_{sample}}{V_{ref}} - 1 \right) S_{Au} \quad (S1)$$

where  $S_{const}$  and  $S_{Au}$  are the Seebeck coefficient of Constantan wire and Au layer. At room temperature,  $S_{const} = -39 \mu V/K$  and  $S_{Au} = 1.49 \mu V/K$ , respectively.

### 3 DFT Calculations

Density functional theory (DFT) calculations at the B3LYP/6-311G(d,p) level were performed using Gaussian 16<sup>9</sup> to gain further insights into the mechanism of proposed doping process. To simplify the calculation, we used only one repeat-unit comprising two cations, which is sufficient to reveal any anomalies in the frontier orbitals. For each molecule, we first optimized the geometry and then performed a single point energy calculation at the same level. For the first protonation step, we calculated the CPI units both in a neutral state (with OH group attached to the tritylium ion, see P-1 in Fig. ??) and in cationic state (refer P-2 and P-3 in Fig. ??). The values in Table S1 are very large because of the lack of solvation. The trend is in agreement with the experimental results.

**Table S1:** Summary of the total energy difference of **CPIZ-T**, **CPIZ-TT**, and **CPIZ-TT-DEG**.

	CPI-(OH) <sub>2</sub>	+	2 H <sup>+</sup>	→	CPI-cation	+	2 H <sub>2</sub> O	ΔE
	(kcal mol <sup>-1</sup> )		(kcal mol <sup>-1</sup> )		(kcal mol <sup>-1</sup> )	+	(kcal mol <sup>-1</sup> )	(kcal mol <sup>-1</sup> )
<b>CPIZ-T</b>	-2475474.11		0		-2380019.17		-95942.92	-487.99
<b>CPIZ-TT</b>	-3168091.483		0		-3072642.05		-95942.92	-493.49
<b>CPIZ-TT-DEG</b>	-3455615.491		0		-3360174.83		-95942.92	-502.26



**Table S2:** Summary of the total energy of **CPIZ-T**, **CPIZ-TT**, and **CPIZ-TT-DEG** in different spin states.

	Close Shell singlet state*	Open shell singlet state	Open Shell triplet state
	(kcal mol <sup>-1</sup> )	( $\Delta E$ kcal mol <sup>-1</sup> )	( $\Delta E$ kcal mol <sup>-1</sup> )
<b>CPIZ-T</b>	0	0.50	29.20
<b>CPIZ-TT</b>	0	0	25.10
<b>CPIZ-TT-DEG</b>	0	0	19.03

\*Set to 0 to allow comparison between polymers.

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