

Supporting Information

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Thermally Activated Aromatic Ionic Dopants (TA-AIDs)
Enabling Stable Doping, Orthogonal Processing and
Direct Patterning

*Zhifan Ke, Mustafa H. Ahmed, Ashkan Abtahi, Shih-Hsin Hsu, Wenting Wu, Michael F. Espenship, Kyle N. Baustert, Kenneth R. Graham, Julia Laskin, Liang Pan, and Jianguo Mei**

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¹Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA

²School of Mechanical Engineering, Purdue University, West Lafayette, IN 47907, USA

³Department of Chemistry, University of Kentucky, Lexington, KY 40506, USA

Table of Content

Section 1. Synthesis of aromatic ionic dopants

Section 2. Synthesis of polydioxothiophenes

Section 3. Synthesis of EDOT-ProDOT-EDOT trimer

Section 4. Thermally activated doping reaction by TA-AIDs

Section 5. High temperature induced doping reaction via dopant migrations and enhanced miscibility

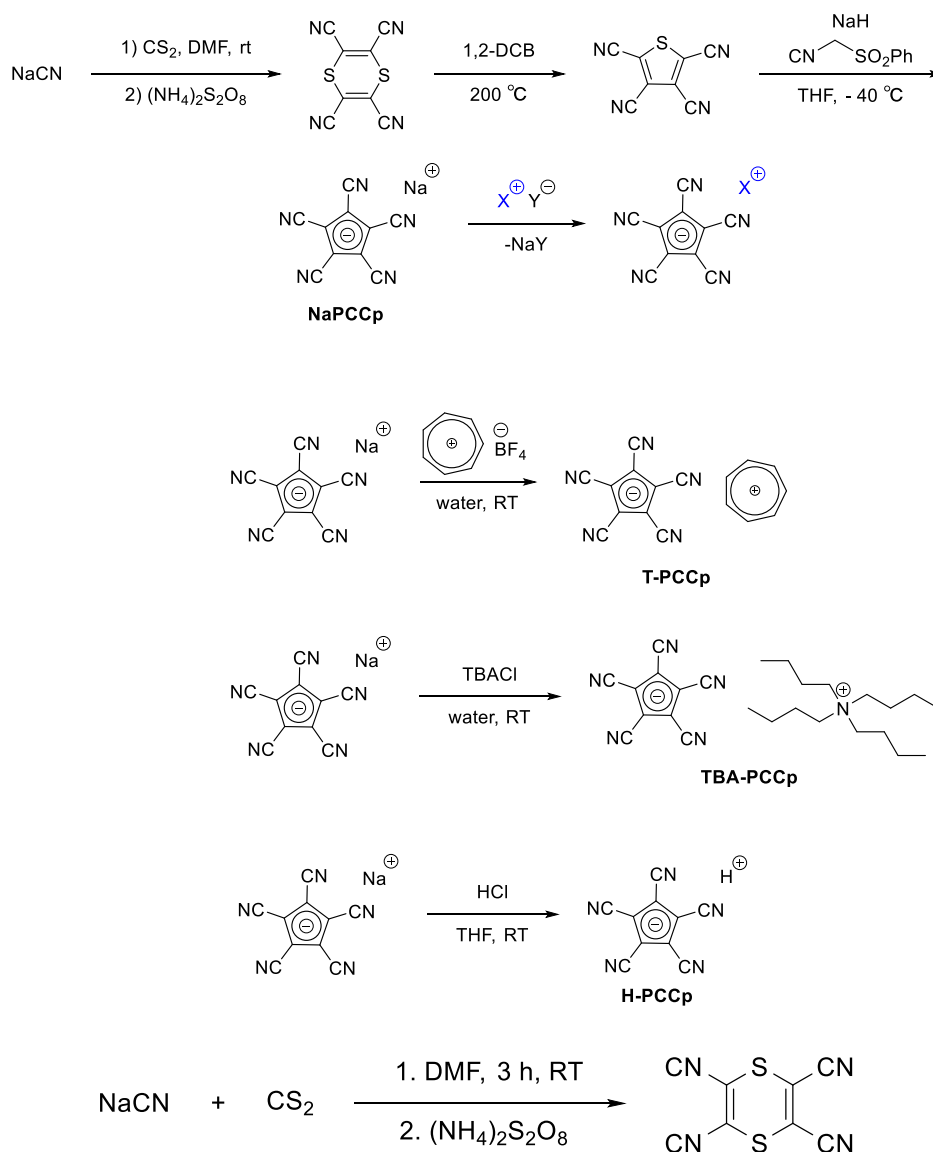
Section 6. Doping mechanisms discussion

Section 7. Pattern conducting polymers by laser direct writing

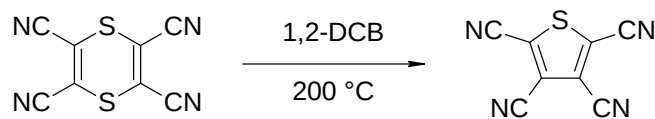
References

From Section 1 to section 3, all reactions were performed under nitrogen atmosphere in oven-dried glassware following standard Schlenk techniques. Anhydrous solvents were purchased from Sigma-Aldrich and used without further purification. Automated preparative chromatography was performed with a Yamazen Smart Flash AI-580S-Premiun. ¹H NMR and ¹³C NMR were recorded on Bruker AV-III-400 and Bruker Avance-III-800 instruments with chemical shifts reported relative to residual solvent. Infrared spectra were measured with a Thermo Nicolet Nexus FT-IR. HRMS data were obtained on an Thermo LTQ-Orbitrapmass spectrometer with a FTMS analyzer. Glass transition temperature, T_g, was measured using a TA Instruments DSC Q 2000.

Section 1. Synthesis of aromatic ionic dopants



Tetracyanodithiin (TCDT) was prepared following literature procedure.^[1] To a suspension of NaCN (23.5 g, 1.0 eq) in DMF (260 mL), CS₂ (28.8 mL, 1.0 eq) was added dropwise via a pressure equalizing dropping funnel. The reaction was stirred at room temperature for 3 h. The reaction was then precipitated into water (1400 mL) and was left undisturbed for 14 h. The precipitated solids were removed by filtration, and the mother liquor was collected into a beaker. To the reaction in the beaker, a solution of ammonium sulfate (109.5 g, 1.0 eq in 210 mL of water) was added dropwise over 40 min. Following addition, the reaction mixture was stirred for an additional 30 min. The resulting solids were collected by filtration, washed with water, and dried. The solids were suspended in MeCN (1400 mL), stirred for 30 min, then filtered. The filtrate was collected and concentrated via rotovap to yield tetracyanodithiin (17.5 g, brown/orange solid) which was used directly in the next step.



Tetracyanothiophene (TCT) was synthesized following literature procedure.^[1] TCDT (6.5 g) was dissolved into 1,2-dichlorobenzene (80 mL) into a 100-mL Schlenk tube. The reaction mixture was degassed by three freeze-pump-thaw cycles via a liquid nitrogen bath. The reaction was then stirred for 2 h at 200 °C. Once cooled, the reaction was poured into hexanes (300 mL) and mixed. The resulting brown solids were collected via filtration. The solids were dissolved into EtOAc (300 mL) and passed through a short plug of silica. The filtered solution was then concentrated via rot evap. The resulting dark brown solid was dissolved in the minimum amount of EtOAc and precipitated into hexanes (300 mL). The resulting brown solids were collected and dried (5.5 g, 83%). ¹³C NMR (101 MHz, CD₃CN): δ ppm 125.5, 122.1, 110.1, 109.9. Analytical data matched reported in the literature. Spectrum shown for purity.

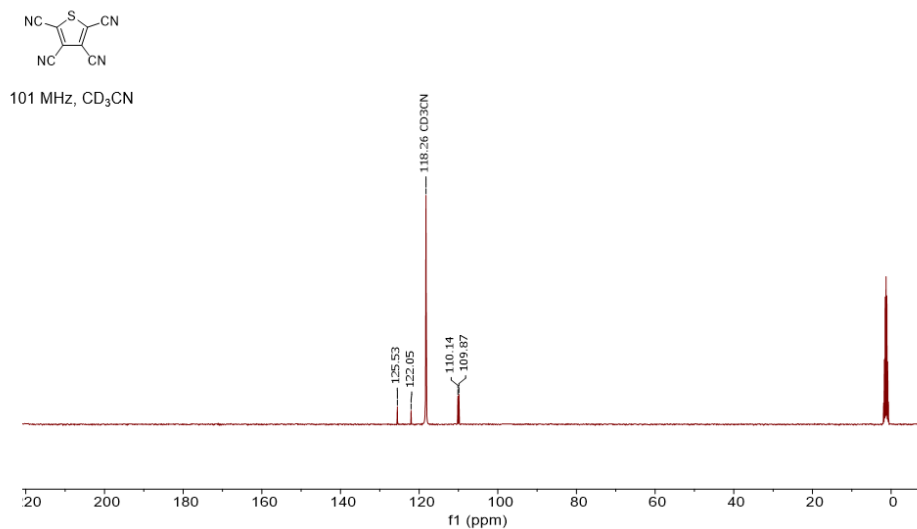
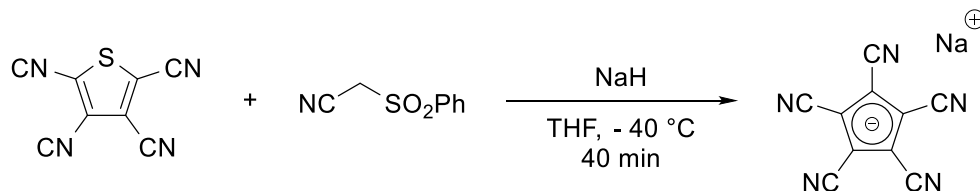


Figure S1. ¹³C NMR of Tetracyanothiophene in CD₃CN.



Sodium Pentacyanocyclopentadienide (NaPCCp) was synthesized following literature procedure.^[1] A suspension of NaH (60% dispersed in mineral oil, 0.66 g, 3.0 eq) in THF (7 mL) was cooled to 0 °C. Once at temperature, a solution of ethyl 2-(phenylsulfonyl)acetate (1.0 g, 1.0 eq in 15 mL THF) was added dropwise. The reaction mixture was stirred at 0 °C for 1 h. The reaction was then cooled to -40 °C. After cooling, a solution of TCT (1.1 g, 1.1 eq) in THF (15 mL) was added dropwise. The reaction was stirred at -40 °C for 40 min. After 40 min, the reaction was quenched with 30 mL of saturated NaCl solution and warmed to RT. The resulting reaction mixture was extracted with EtOAc. The organic phase was washed with brine, dried with Na₂SO₄, and concentrated via rot evap. The reaction was then passed through a short silica plug (90/10 EtOAc/MeCN). The collected reaction was then concentrated. The dark

brown solid was then dissolved in the minimum amount of MeCN and precipitated into dichloromethane (300 mL). The resulting precipitates were collected by filtration and dried as a light brown solid (1.09 g, 92%). ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 113.02, 101.73. Analytical data matched reported in the literature. Spectrum shown for purity

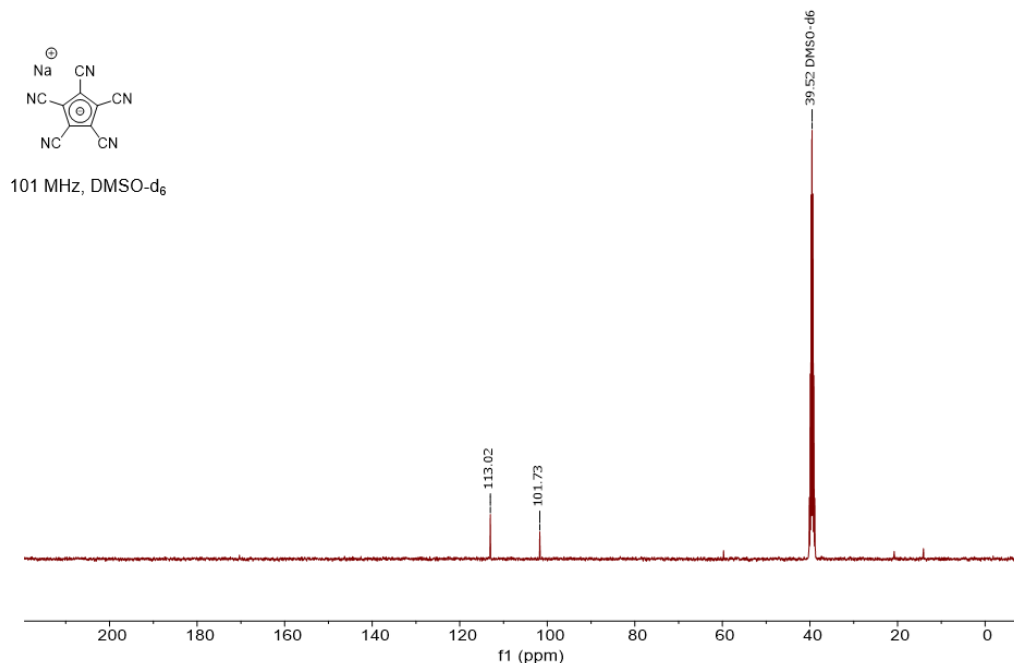
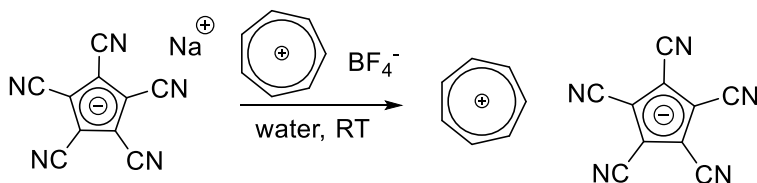


Figure S2. ^{13}C NMR of NaPCCp in DMSO-d_6 .



Tropylium Pentacyanocyclopentadienide (T-PCCp) was synthesized following literature procedure.^[2] A solution of NaPCCp (1.0 g, 1.0 eq) in water (9 mL) was added to a solution of Tropylium Tetrafluoroborate (0.84 g, 1.0 eq) in water (9 mL). The resulting solution was mixed to precipitate a greenish brown solid. The solids were collected via filtration and washed with water. The resulting precipitate were dried thoroughly as a green solid (1.23 g, 93%). ^1H NMR (400 MHz, CD_3CN) δ ppm 9.22 (s, 3H); ^{13}C NMR (101 MHz, CD_3CN) δ ppm 156.2, 114.11, 103.1. Analytical data matched reported in the literature. Spectra shown for purity

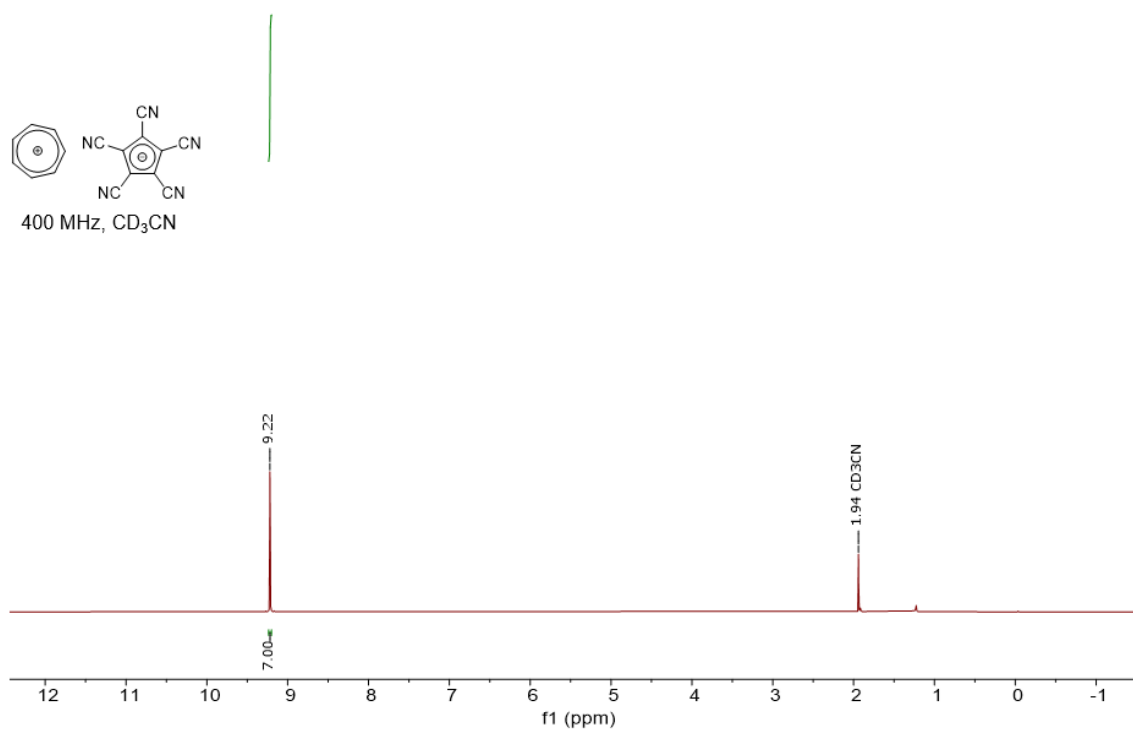


Figure S3. ¹H NMR of T-PCCp in CD₃CN.

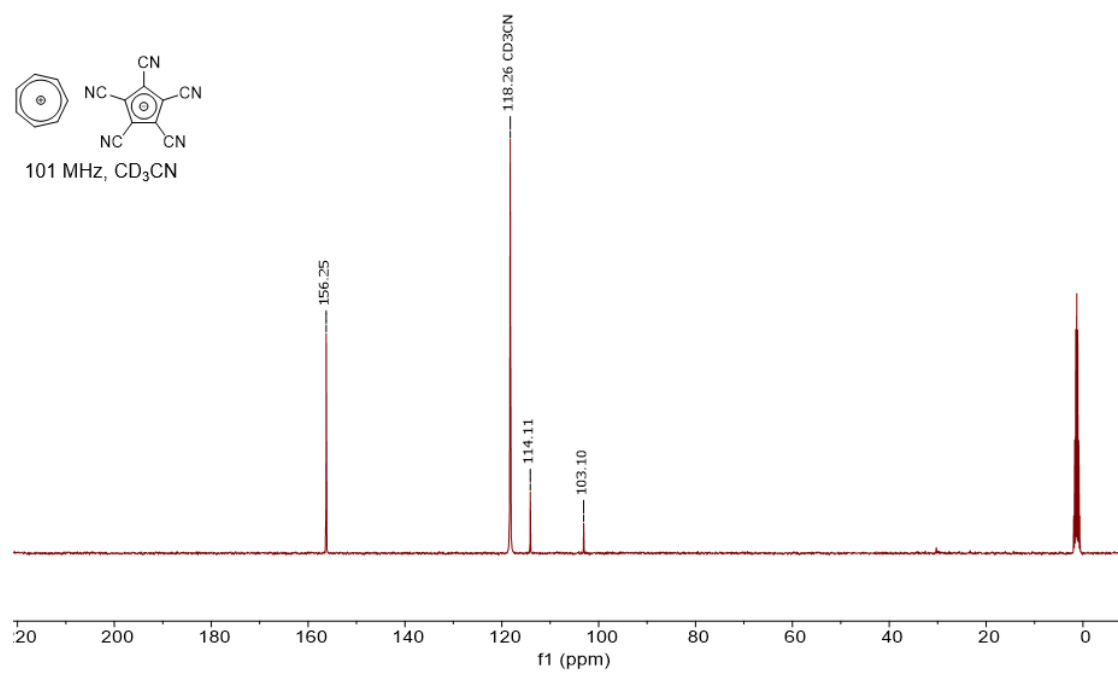
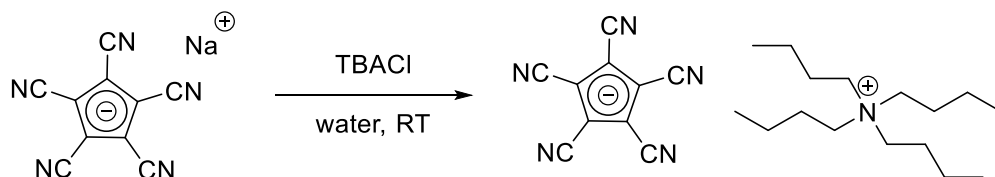


Figure S4. ¹³C NMR of T-PCCp in CD₃CN.



Tetrabutylammonium Pentacyanocyclopentadienide (TBA-PCCp) was synthesized following literature procedure.^[2] A solution of NaPCCp (1.0 g, 1.0 eq) in water (9 mL) was added to a solution of tetrabutylammonium (TBA) chloride (1.27 g, 1.0 eq) in water (9 mL). The resulting solution was mixed to precipitate an orange solid. The solids were collected via filtration and washed with water. The resulting precipitate was dried thoroughly as an orange solid (1.15 g, 96%). ¹H NMR (400 MHz, CDCl₃) δ ppm 3.18 – 3.14 (m, 8 H), 1.69 – 1.61 (m, 8H), 1.46 (m, 8H), 1.03 (t, 12 H); ¹³C NMR (101 MHz, CDCl₃) δ 113.7, 102.6, 59.1, 23.9, 19.8, 13.6. Analytical data matched reported in the literature. Spectra shown for purity.

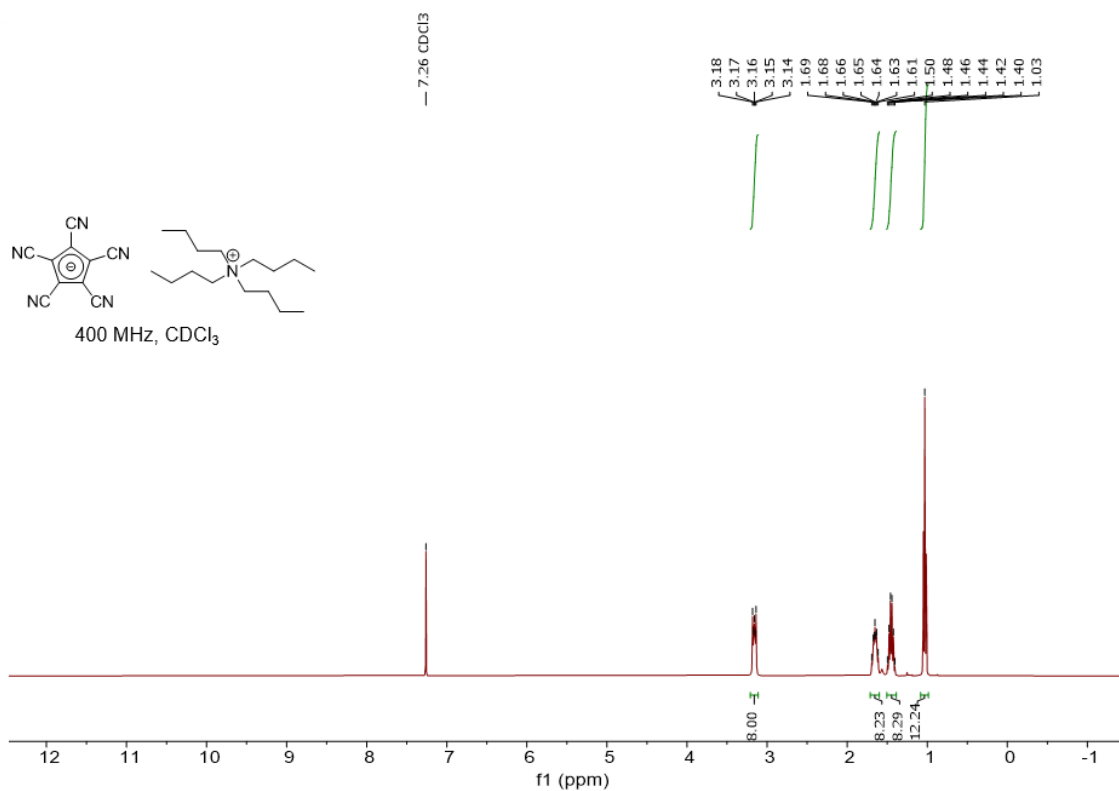


Figure S5. ¹H NMR of TBA-PCCp in CHCl₃

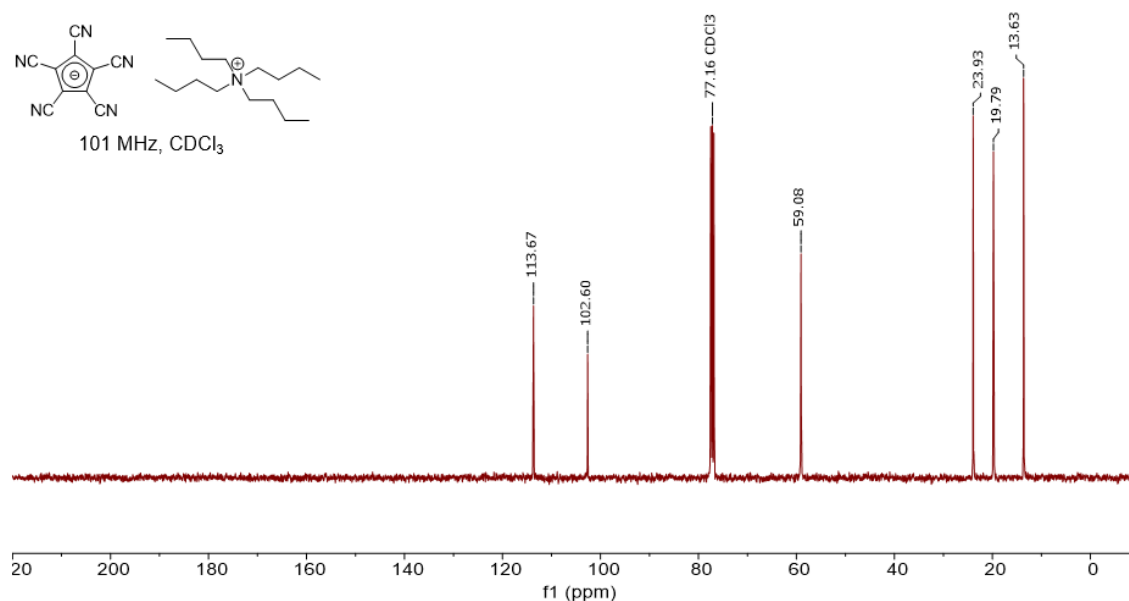
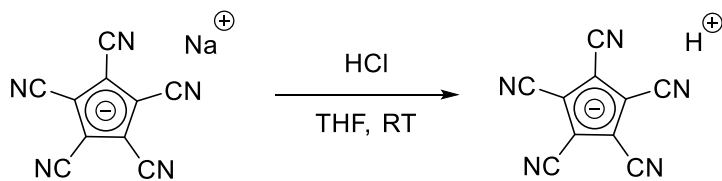


Figure S6. ^{13}C NMR of TBA-PCCp in CHCl_3



Hydrogen Pentacyanocyclopentadienide (H-PCCp) was synthesized by the following procedure: 4N HCl in 1,4-dioxane (130 μL , 1.1 eq) was added to a solution of NaPCCp (100 mg, 1.0 eq) in THF (1 mL). The resulting solution was mixed to precipitate a brown/yellow solid. The solids were removed via filtration and the yellow filtration was collected. Removing the solvent *in vacuo*, resulted in a brown syrup that solidified over several days as a brown solid (69.9 mg, 78%). ^1H NMR (400 MHz, CD_3CN): δ ppm 8.20 (H^+); ^{13}C NMR (101 MHz, CD_3CN): δ ppm 103.1, 67.6. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. For C_{10}HN_5 190.01530, Found 190.01608.

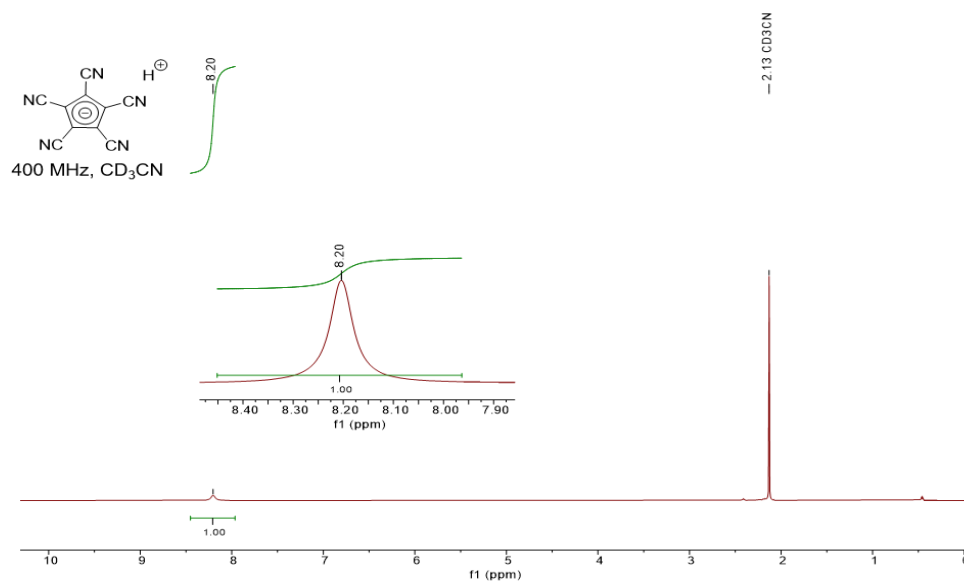


Figure S7. ¹H NMR of H-PCCP in CD₃CN

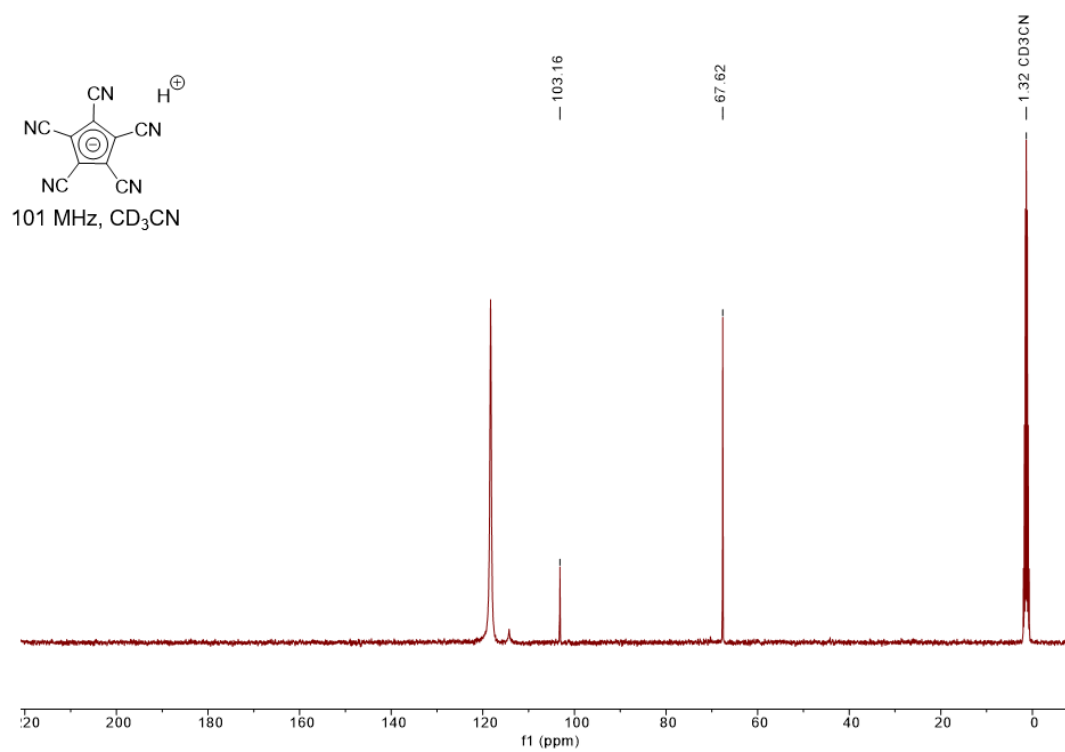
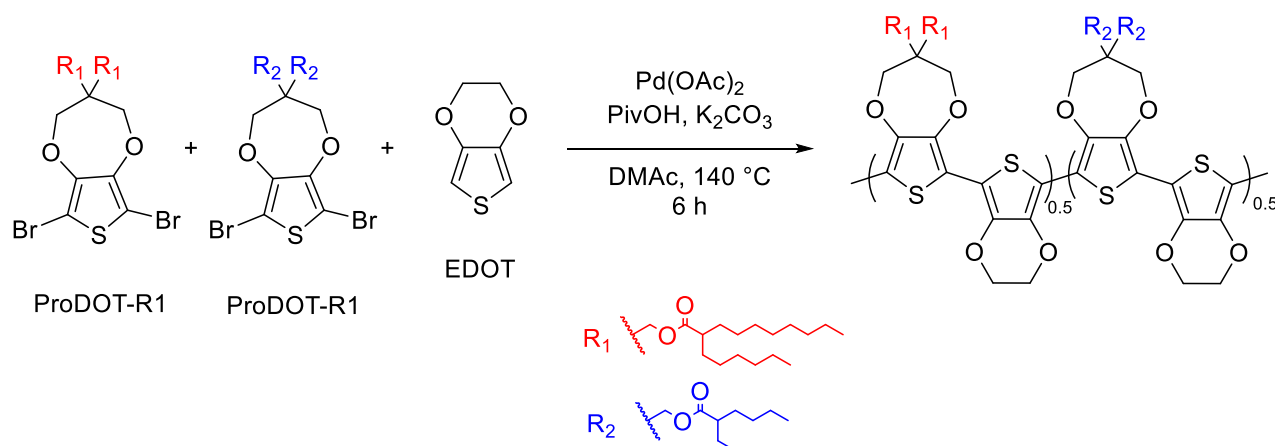


Figure S8. ¹³C NMR of H-PCCP in CD₃CN.

Section 2. Synthesis of polydioxothiophenes



Polydioxythiophene: P1 was synthesized according to the following procedure^[3]: ProDOT-R1 (0.5 eq.), ProDOT-R2 (0.5 eq.), EDOT (1.0 eq.), K_2CO_3 (2.6 eq.), PivOH (0.3 eq.) and Pd(OAc)_2 (0.02 eq) were added to a Schlenk flask, kept under vacuum for about 15 min and purged with nitrogen, three times. Then, nitrogen degassed solvent DMAc (30 ml of solvent for 1.0 g of EDOT) was added to the flask and heated in an oil bath at 140 °C for 6 h under nitrogen. The hot reaction mixture was precipitated to a 1:1 mixture of CH_3OH and 1 M HCl while stirring. The resulting mixture was filtered to obtain a solid. This solid was further dissolved in chloroform and washed with 1 M HCl solution. The organic phase was concentrated and precipitated with acetone, filtered, and dried to obtain the polymer (95% yield). ^1H NMR (800 MHz, CDCl_3) δ ppm 4.60–4.25 ($\text{CH}_2\text{-O}$), 2.38 (CHC=O), 1.32–1.20 (CHCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.93–0.87 (CH_2CH_3).

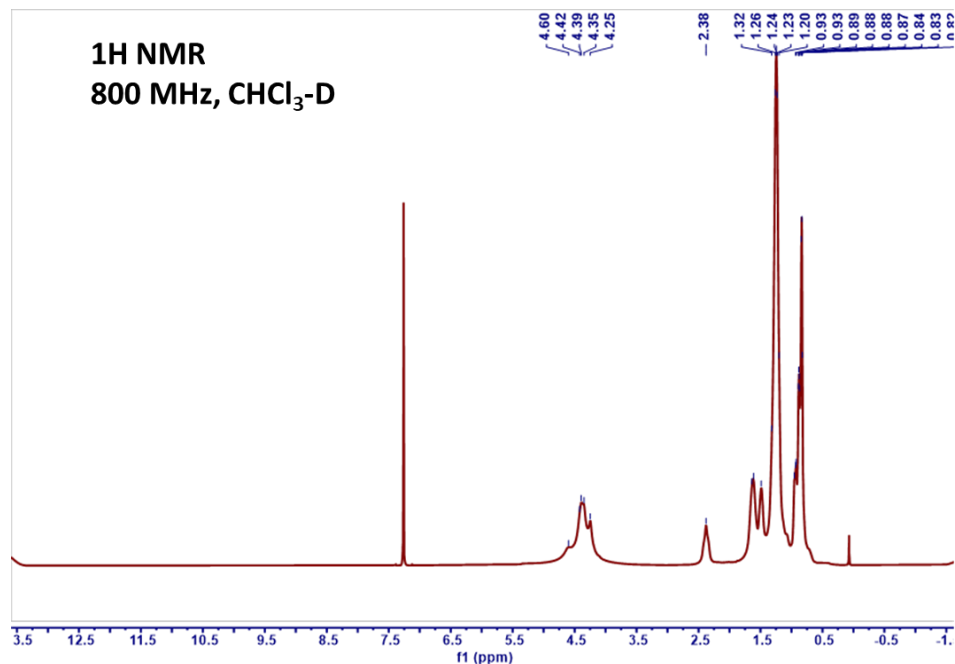
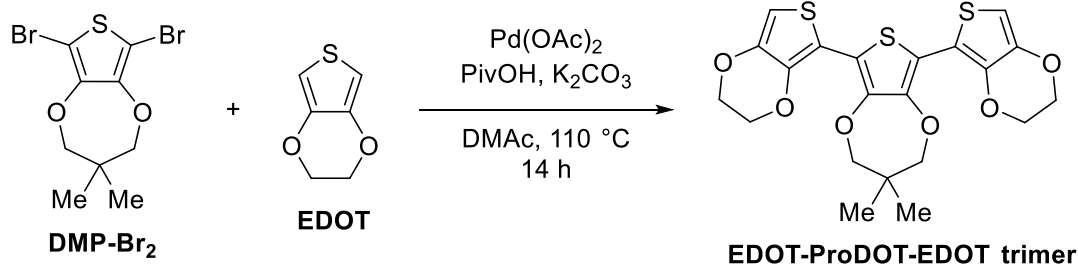


Figure S9. ^1H -NMR spectrum for P1 in CDCl_3 .

Section 3. Synthesis of EDOT-ProDOT-EDOT trimer



6,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (EDOT-ProDOT-EDOT trimer) was synthesized according to the following procedure: An oven dried Schlenk tube was charged with Pd(OAc)₂ (197 mg, 0.87 mmol), PivOH (268 mg, 2.63 mmol), 6,8-dibromo-2,2-dimethyl ProDOT (DMP-Br₂) (3.0 g, 8.8 mmol), and EDOT (12.47 g, 87.7 mmol). The reaction vessel was then evacuated and backfilled with nitrogen for three times. The Teflon screw cap was replaced with a rubber septum and approximately 10 mL of anhydrous DMAC was added. The Schlenk tube was then purged with nitrogen for 2 minutes and the rubber septum was replaced with a Teflon screw cap. The Schlenk tube was then placed in an oil bath at 110 °C for 14 hours. After completion of the reaction, the solvent was removed, and the crude reaction was extracted with dichloromethane. The organic layer was dried with Na₂SO₄, filtered, and concentrated via rotary evaporator. The reaction mixture was purified by flash column chromatography on silica gel (gradient elution: 1:1-1:2 Hexanes/DCM) to afford 1.25 g of trimer as pale-yellow solid (31% yield). ¹H NMR (400 MHz, THF-d₈) δ ppm 6.27 (s, 2H), 4.33–4.26 (m, 4H), 4.22–4.15 (m, 4H), 3.78 (s, 4H), 1.06 (s, 6H); ¹³C NMR (100 MHz, toluene-D₈): δ ppm 145.5, 141.8, 137.7, 114.1, 111.5, 98.1, 80.0, 64.9, 64.3, 38.7, 21.3; IR (neat, cm⁻¹): 3096, 2917, 2866, 1582, 1554, 1516, 1419; HRMS (APCI) ([M+H]⁺) Calcd. For C₂₁H₂₁O₆S₃ 465.0495, Found 465.0499.

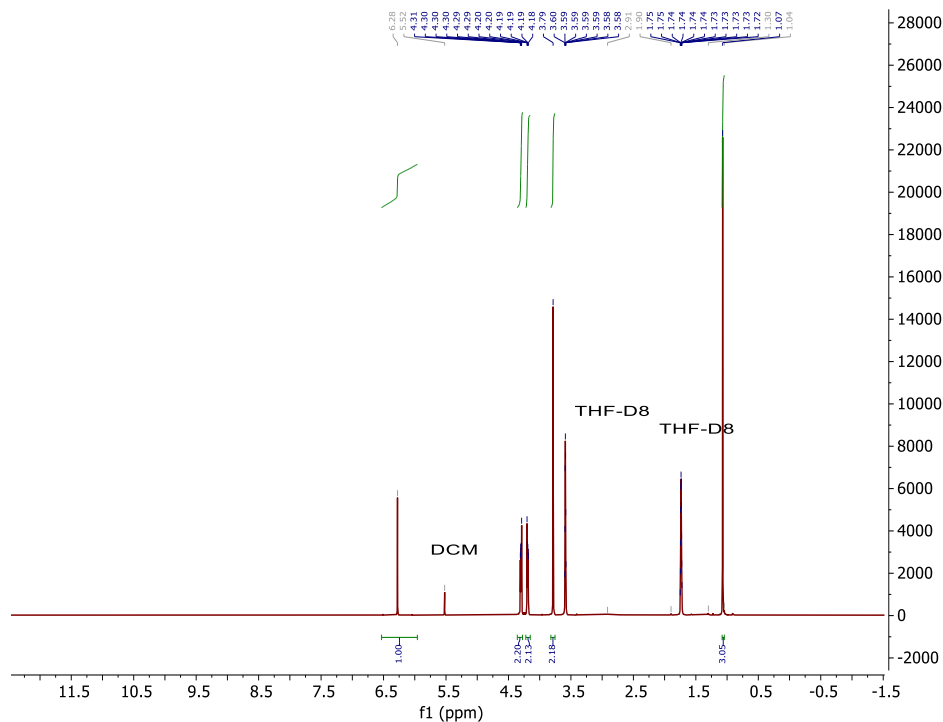


Figure S10. ¹H-NMR spectrum for **EDOT-ProDOT-EDOT trimer** in THF-d₈.

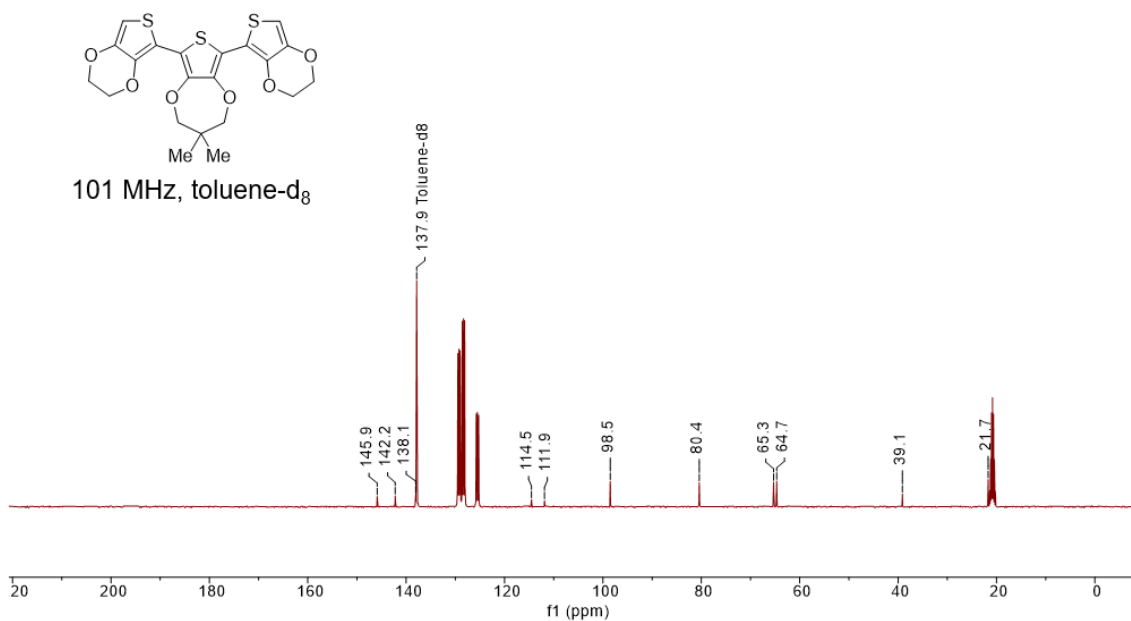


Figure S11. ¹³C-NMR spectrum for **EDOT-ProDOT-EDOT trimer** in toluene-d₈.

T: FTMS + p APCI corona Full ms [150.00-800.00]

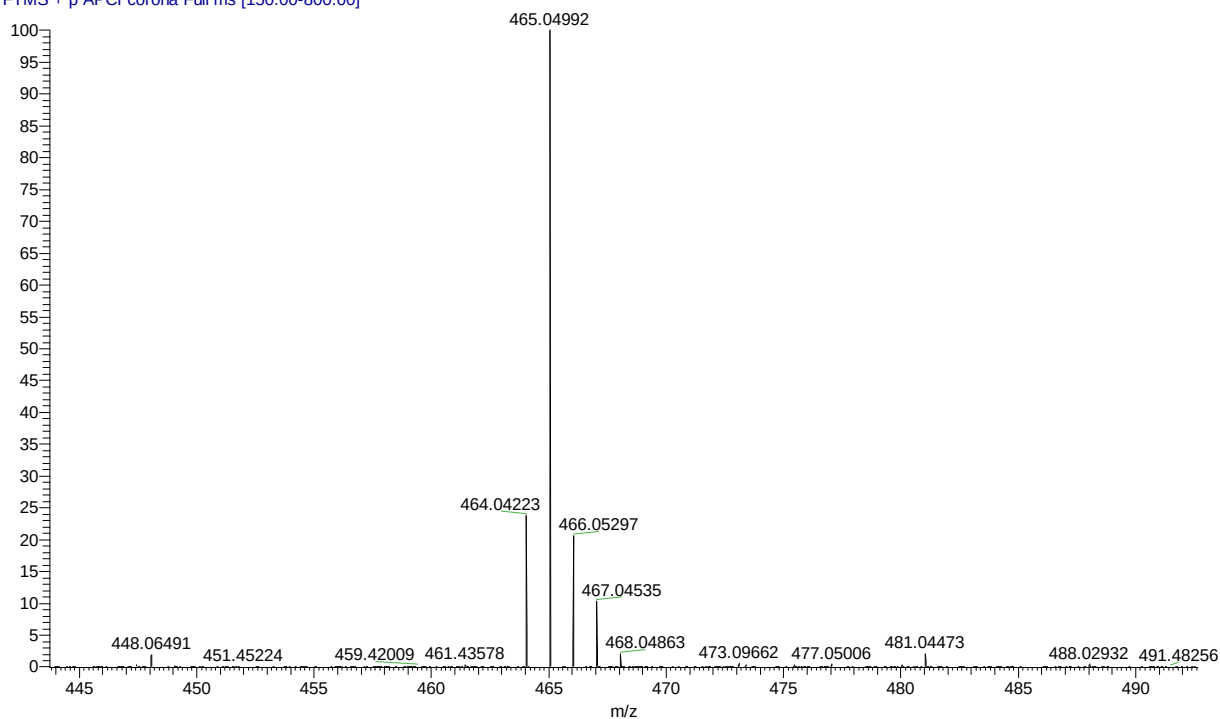


Figure S12. High-resolution mass spectrometry for trimer. 100μM trimer is dissolved in mixed methanol-dichloromethane (70:30, %v/v) solvent.

Section 4. Thermally activated doping reaction by TA-AIDs

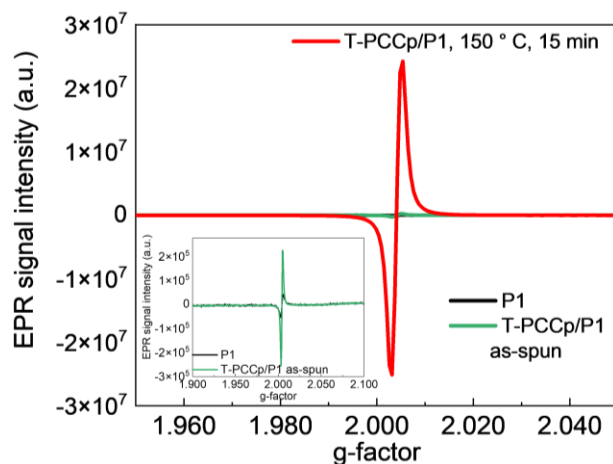


Figure S13. EPR spectra for pristine P1, as-casted T-PCCp/P1 and annealed T-PCCp/P1 solid samples. Pristine P1(black) shows a weak EPR signal because P1 can be slightly doped by air, as-casted T-PCCp/P1(green) show lightly increased signal intensity and annealed sample show greatly improved signal intensity (red). The higher intensity after thermal annealing in comparison to as-cast sample indicates thermal activated doping reaction.

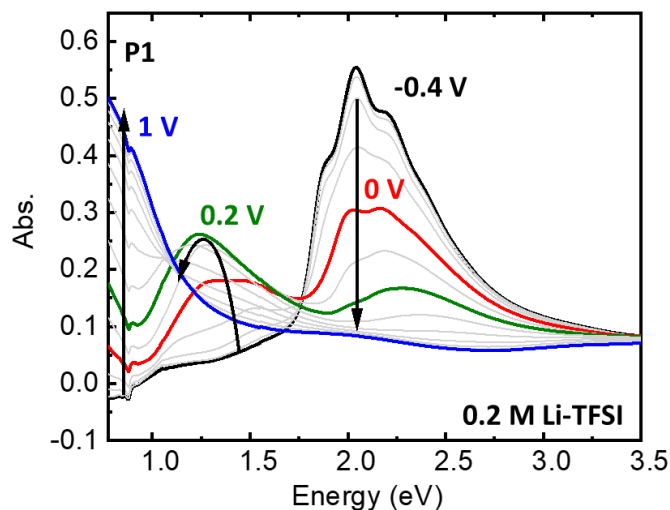


Figure S14. Spectroelectrochemical spectra of P1 in 0.2 M Li-TFSI propylene carbonate (PC) solution. The black line, red line, green line and blue line represent the absorption of P1 under -0.4 V, 0V, 0.2 V and 1 V vs Ag/AgCl potential, respectively.

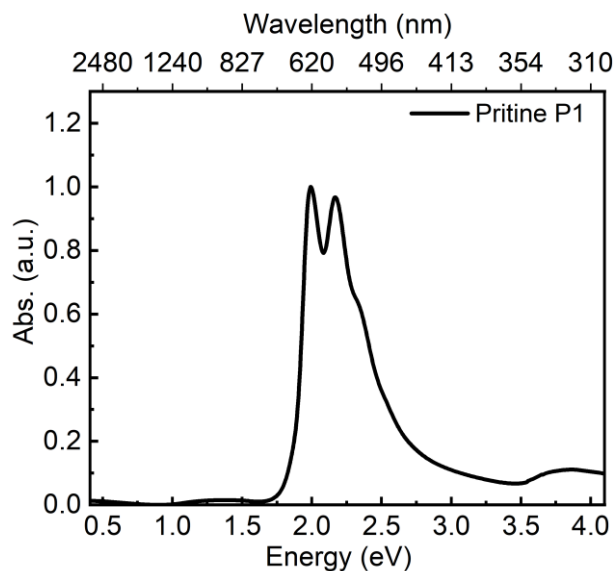


Figure S15. UV-vis absorption spectra of pristine P1, with the neutral peak around 2.25 eV(550nm).

Table S1. Average Conductivity of T-PCCp/P1 annealed at different conditions, the unit of conductivity is S/cm.

	20 °C	50 °C	100 °C	150 °C	200 °C	250 °C
5 seconds	0.001	0.006	0.32	18.6	67.4	28.1
30 seconds	0.001	0.017	2.16	39.2	128.9	27.3
1 minute	0.001	0.063	5.28	48.4	76.4	15.3
5 minutes	0.001	0.087	14.4	49.7	53.7	13.8
15 minutes	0.001	0.112	37.7	67.8	49.4	4.4
30 minutes	0.001	0.226	49.3	87.4	31.1	3.2

Table S2. The average thickness comparison between H-PCCp, TBA-PCCp, T-PCCp and T-BF₄ doped P1

Samples	Average thickness (nm)
H-PCCp/P1	130 nm
TBA-PCCp/P1	125 nm
T-PCCp/P1	120 nm
T-BF ₄ /P1	120 nm

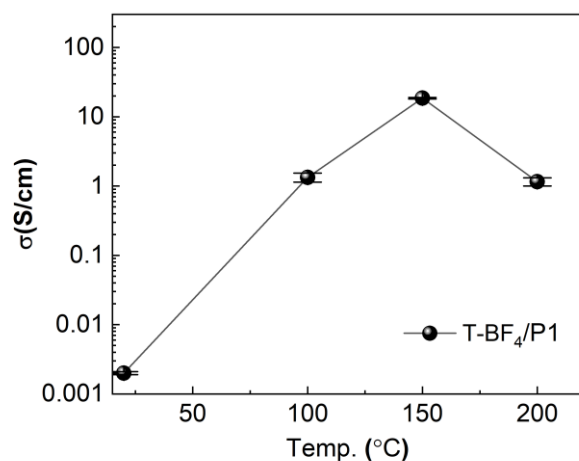


Figure S16. Conductivity of T-BF₄/P1 processed at different thermal annealing temperatures for 15 minutes.

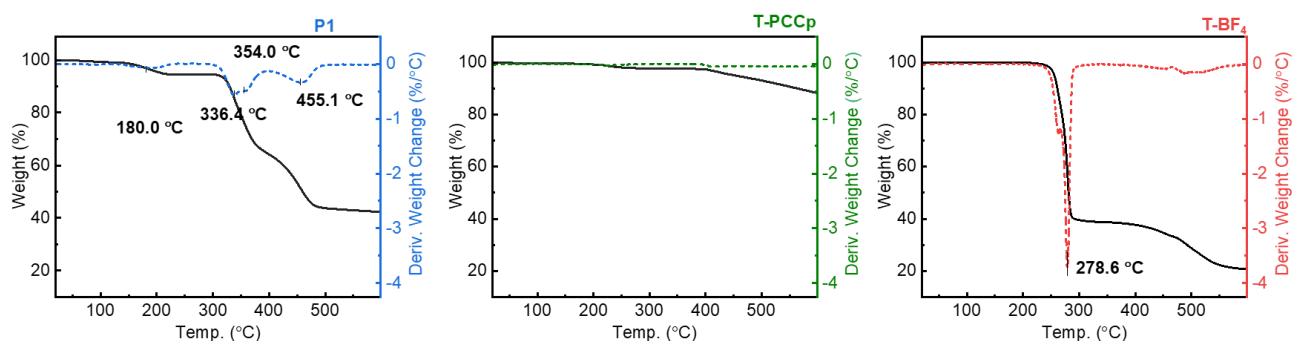


Figure S17. Thermogravimetric analysis of pure P1, T-PCCp and T-BF₄.

Section 5. High temperature induced doping reaction via dopant migrations and enhanced miscibility

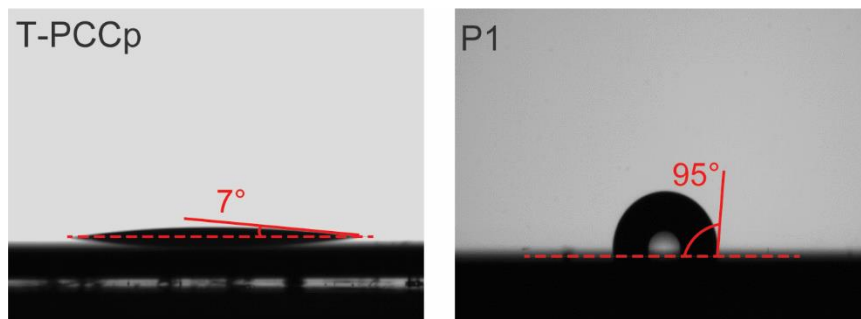


Figure S18. Water contact angle measurement of T-PCCp and P1 thin film coated on glass slide.

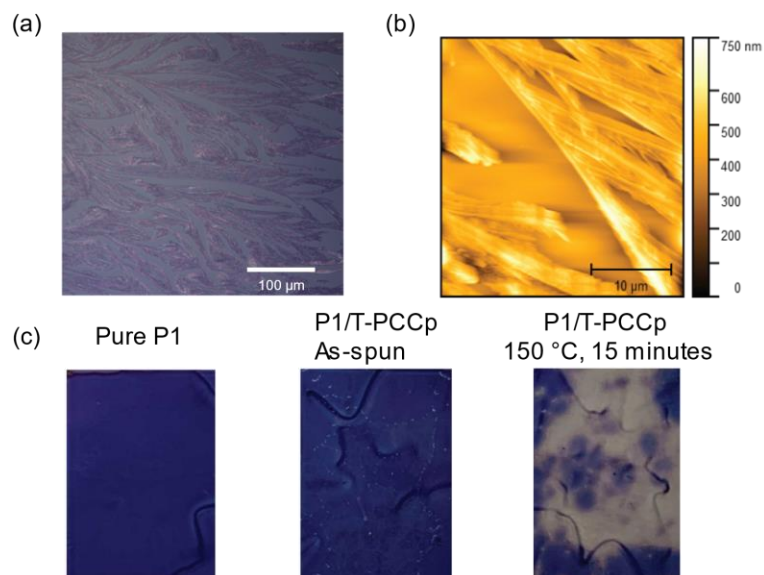


Figure S19. P1 was firstly spin-casted on clean substrates from a chloroform solution of 20 mg/mL, and T-PCCp was deposited from acetonitrile solution on the top of P1 layer. T-PCCp cannot for a uniform layer on P1, shown in the photo (a) and AFM (b) images. Due to the uneven distribution of T-PCCp, after thermal annealing only part of the thin film got doped. In (c), the bleached part showed the doped region while the blue part still maintained undoped.

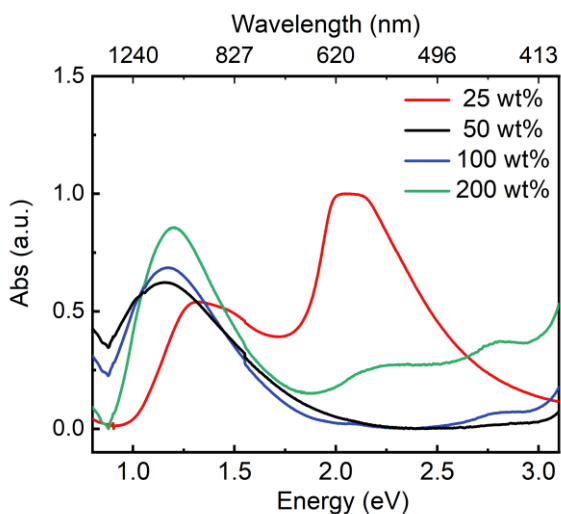


Figure S20. UV-Vis NIR spectrum of T-PCCp/P1 mixed solutions with different T-PCCp concentration.

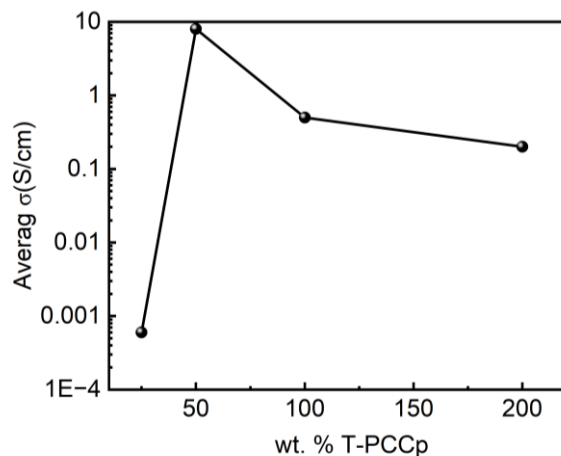


Figure S21. Conductivity of T-PCCp doped P1 thin films casted from T-PCCP/P1 solution mixtures with different dopant concentration.

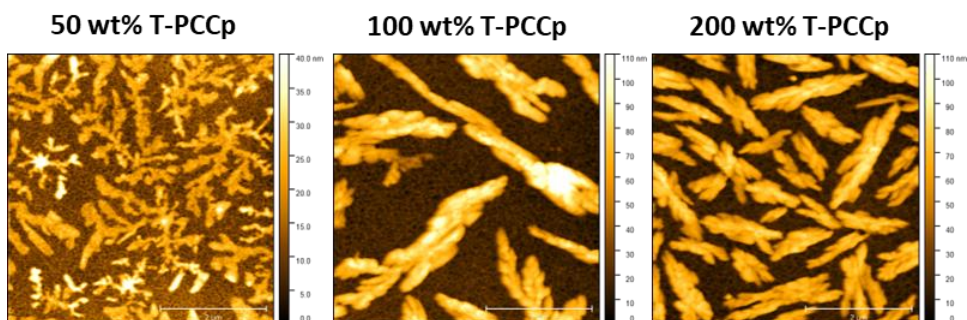


Figure S22. AFM images of T-PCCp doped P1 thin films with different dopant concentration. The thin films were casted from T-PCCp/P1 mixed solution and then annealed at 150 °C for 15 minutes.

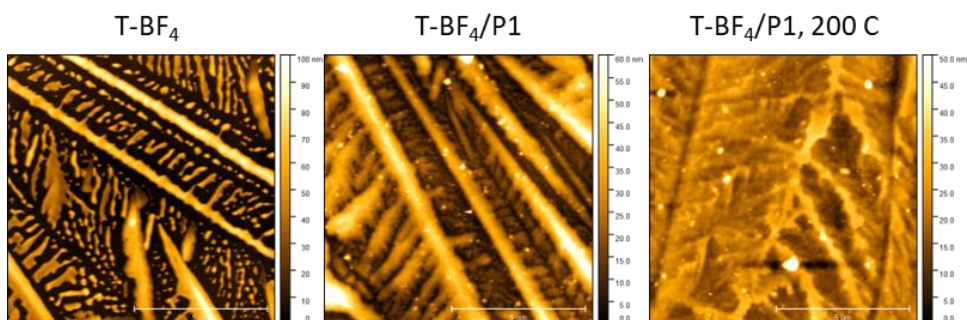


Figure S23. AFM images of T-BF₄, as-prepared T-BF₄/P1 and T-BF₄/P1 after thermal annealing at 200 °C for 30 seconds.

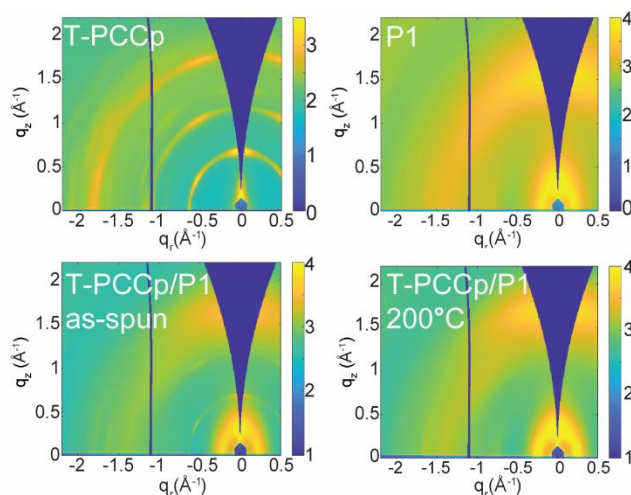


Figure S24. 2D GIXD patterns of pure T-PCCp, as-casted T-PCCp/P1 and T-PCCp/P1 annealed at 200 °C for 30 seconds.

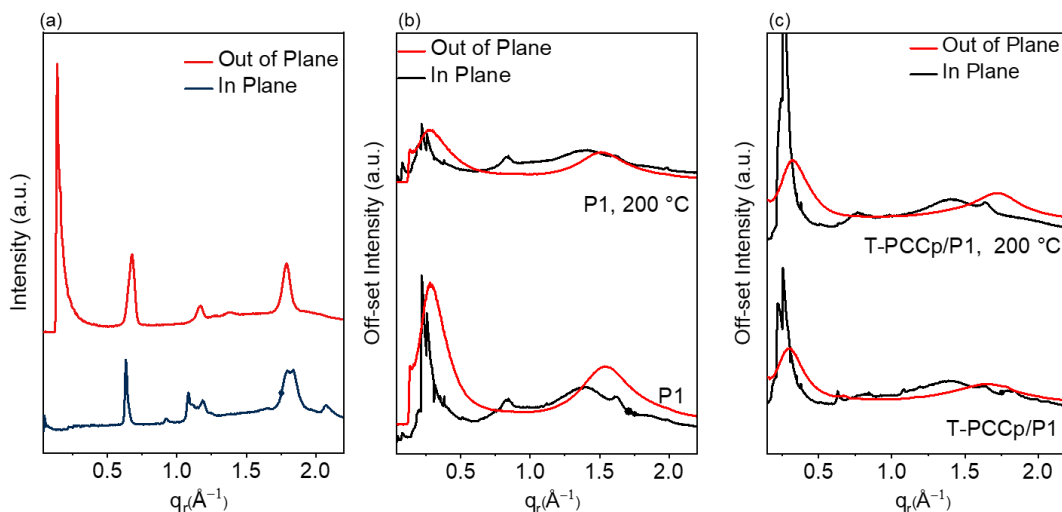


Figure S25. In plane and out of plane GIXD intensity for (a) T-PCCp, (b) P1 without and with thermal annealing; (c) T-PCCp/P1 without and with thermal annealing.

Table S3. Summary of peak position, stacking distance and coherence length (CL) of P1 in pure P1 thin film without and with thermal annealing, T-PCCp/P1 thin film without and with thermal annealing. The coherence length is calculated from Scherrer equation. The coherence length (CL) is calculated via the Scherrer equation: $CL = 2\pi K / \text{FWHM}$, where K is a shape factor (here uses 0.9).^[4]

	In-plane (q_{xy})						Out-of-plane (q_z)					
	π - π stacking			Alkyl-chain stacking			Lamellar stacking			π - π stacking		
	$\text{\AA}^{-1}$	$\text{\AA}$	CL (nm)	$\text{\AA}^{-1}$	$\text{\AA}$	CL (nm)	$\text{\AA}^{-1}$	$\text{\AA}$	CL (nm)	$\text{\AA}^{-1}$	$\text{\AA}$	CL (nm)
P1	1.63	3.85	7.6	0.83	7.7	4.9	0.29	21.8	3.4	1.54	4.1	1.5
P1, 200 °C	1.63	3.85	7.3	0.83	7.7	4.9	0.28	22.0	4.3	1.54	4.1	1.6
T-PCCp/P1	1.64	3.83	6.3	0.80	7.8	3.6	0.31	20.3	3.1	1.65	3.8	1.4
T-PCCp/P1, 200 °C	1.64	3.81	9.2	0.78	8.0	1.1	0.31	19.8	3.8	1.71	3.6	1.8

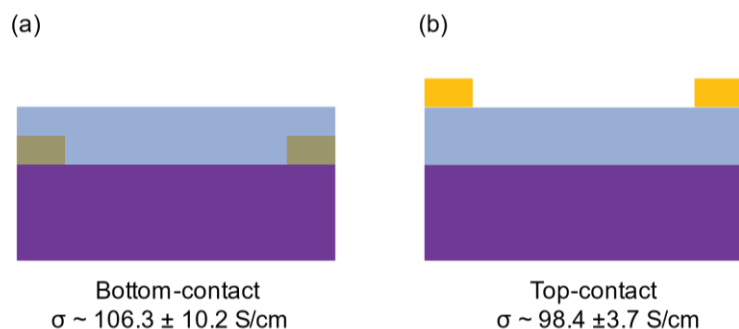


Figure S26. (a) Bottom-contact device configuration for conductivity measurement. T-PCCp and P1 are sequentially deposited on the top of Si/SiO₂ substrate with prepatterned Au electrodes. After being annealed at 200 °C for one minute, the averaged conductivity is 106.3 ± 10.2 S/cm. (b) Top-contact device configuration for conductivity measurement. T-PCCp and P1 are sequentially deposited on bare Si/SiO₂ substrate and then the thin film was annealed at 200 °C for one minute. After that, gold was slowly deposited on the top of the T-PCCp/P1 thin film. The averaged conductivity is 98.4 ± 3.7 S/cm.

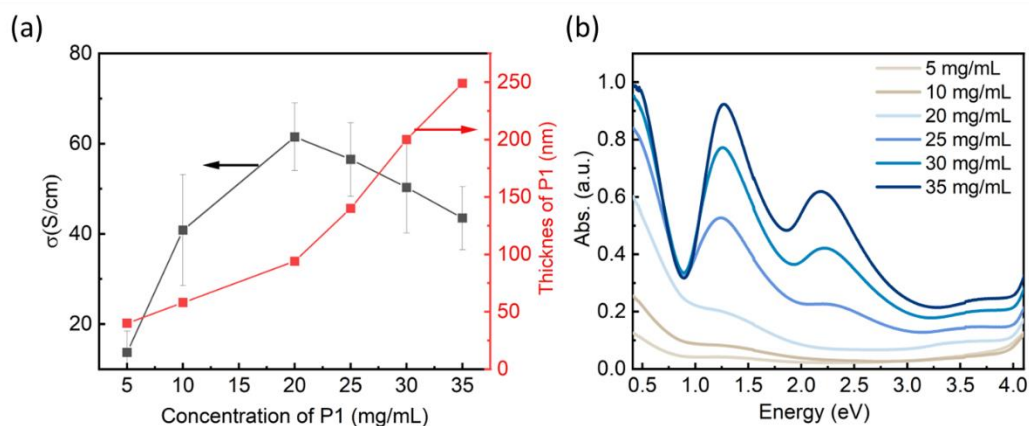


Figure S27. (a) Thickness of pure P1 thin film can be tuned by changing the solution concentration. T-PCCp/P1 with different-thickness P1 is prepared. All the films were thermal annealed at 150 °C for 15 minutes before their conductivities were compared. When the concentration of P1 is 20 mg/mL, the conductivity reaches the maximum number. (b) UV-vis-NIR absorption of T-PCCp/P1 with different-thickness P1. All the samples were thermal annealed at 150 °C for 15 minutes.

Table S4. The average thickness of T-CCp/P1 thin films prepared from P1 solution with different concentrations.

Concentration of P1 (mg/mL)	Average thickness (nm) of T-PCCp/P1
5	85 nm
10	100 nm
20	120 nm
25	200 nm
30	250 nm
35	295 nm

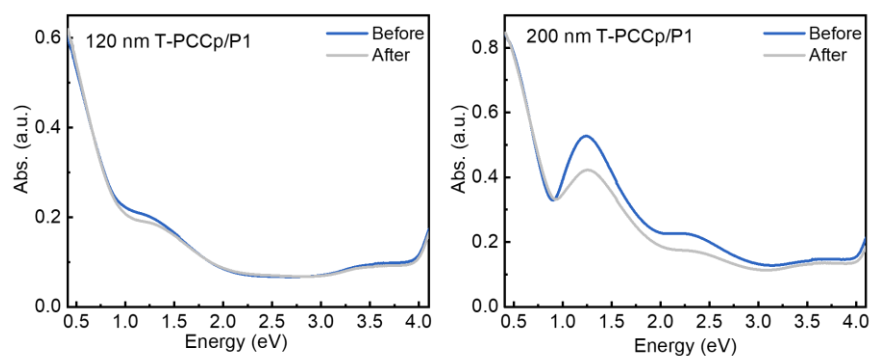


Figure S28. UV-vis-NIR absorption of annealed T-PCCp/P1 with thickness of 120 nm and 200 nm, spin casted from 20 mg/mL and 25 mg/mL P1 chloroform solution. The blue line and gray line represent the absorption of T-PCCp/P1 conductors before and after washed by chloroform, respectively.

Section 6. Doping mechanism discussion

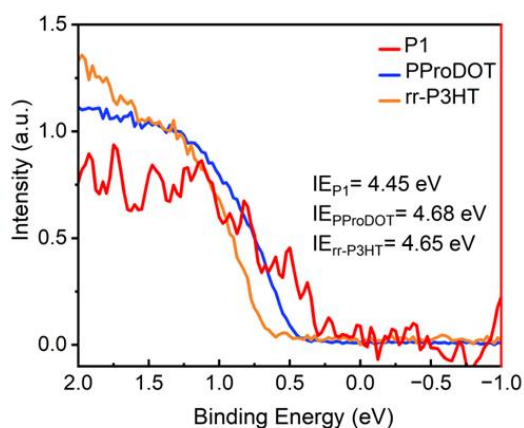


Figure S29. HOMO onset region of P1, PProDOT and rr-P3HT measured by UPS.

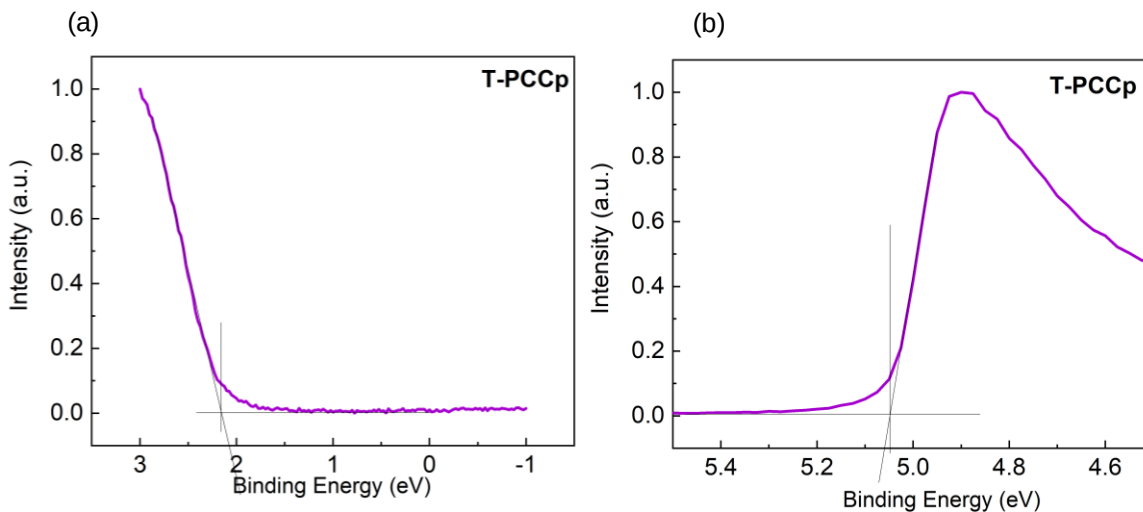


Figure S30. (a) HOMO onset region and (b) secondary cutoff region of T-PCCp measured by UPS.

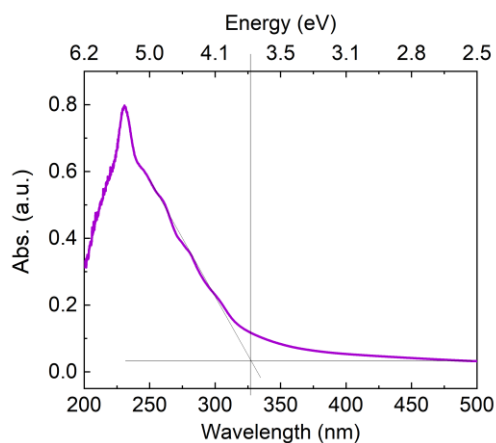


Figure S31. UV-vis spectrum of T-PCCp. The optical band gap of T-PCCp is 3.75 eV and the EA is 3.63 eV, calculated from the onset.^[5]

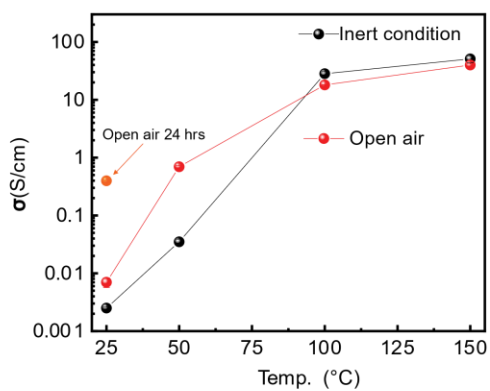


Figure S32. Conductivity comparison between conductive T-PCCp/P1 prepared in inert conditions and in open air with different thermal annealing temperature for 15 minutes. Especially, the orange point, with

the average conductivity ~ 0.33 S/cm, indicates the conductivity of T-PCCp/P1 prepared in the open air and stored for 24 hours, without thermal annealing.

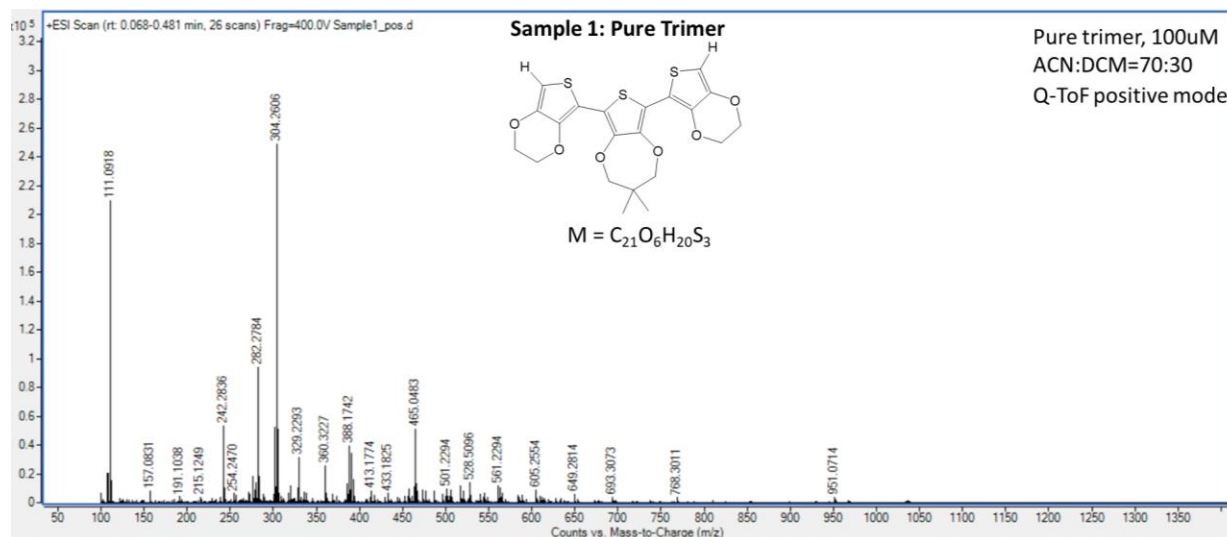


Figure S33. Mass spectrum of pure EDOT-ProDOT-EDOT trimer, showing a hydrogen adduct seen at m/z 465.

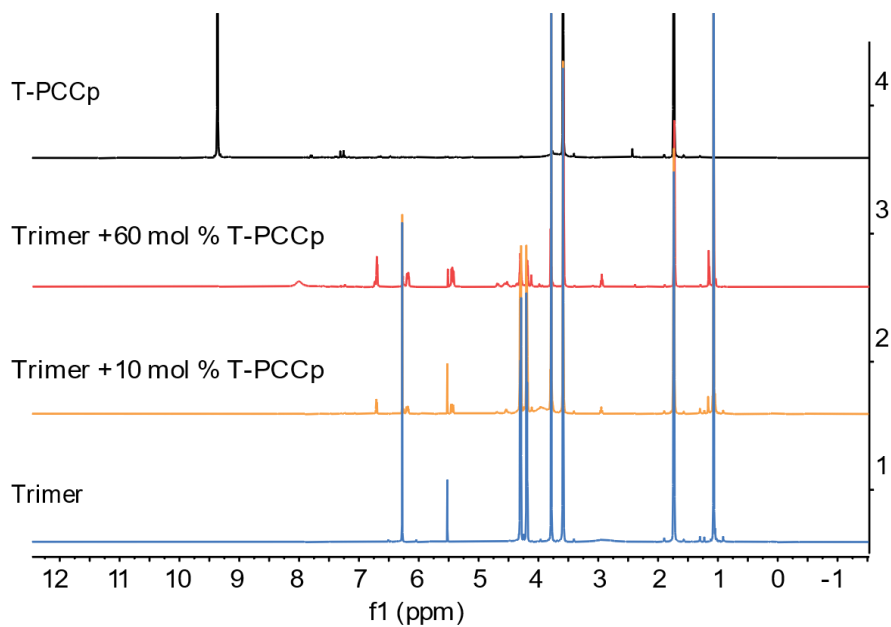


Figure S34. ^1H NMR comparison of pure T-PCCp, trimer with 60 mol% T-PCCp, trimer with 10 mol% T-PCCp and pure trimer.

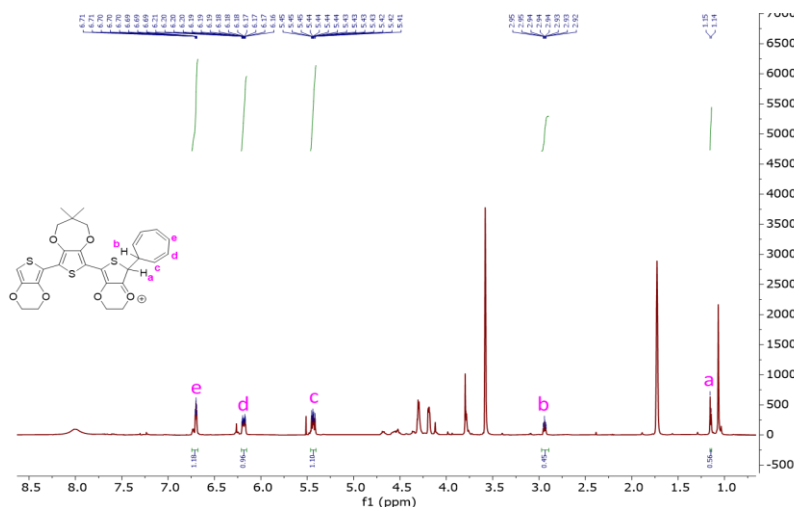


Figure S35. ^1H NMR analysis of trimer with 60 mol% T-PCCp

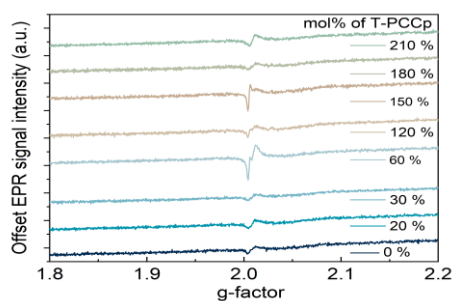


Figure S36. EPR of T-PCCp/trimer mixture solution with the dopant concentration increasing from 0 mol % to 210 mol %.

Section 7. Pattern conducting polymers by laser direct writing

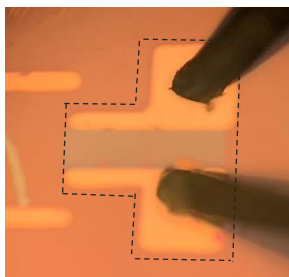


Figure S37. Four 50 μm *50 μm squares were written to form a large 50 μm *200 μm rectangle and its conductivity was measured by using a two-probe method. During measurement the conductive area was isolated as indicated by the black dashed line.

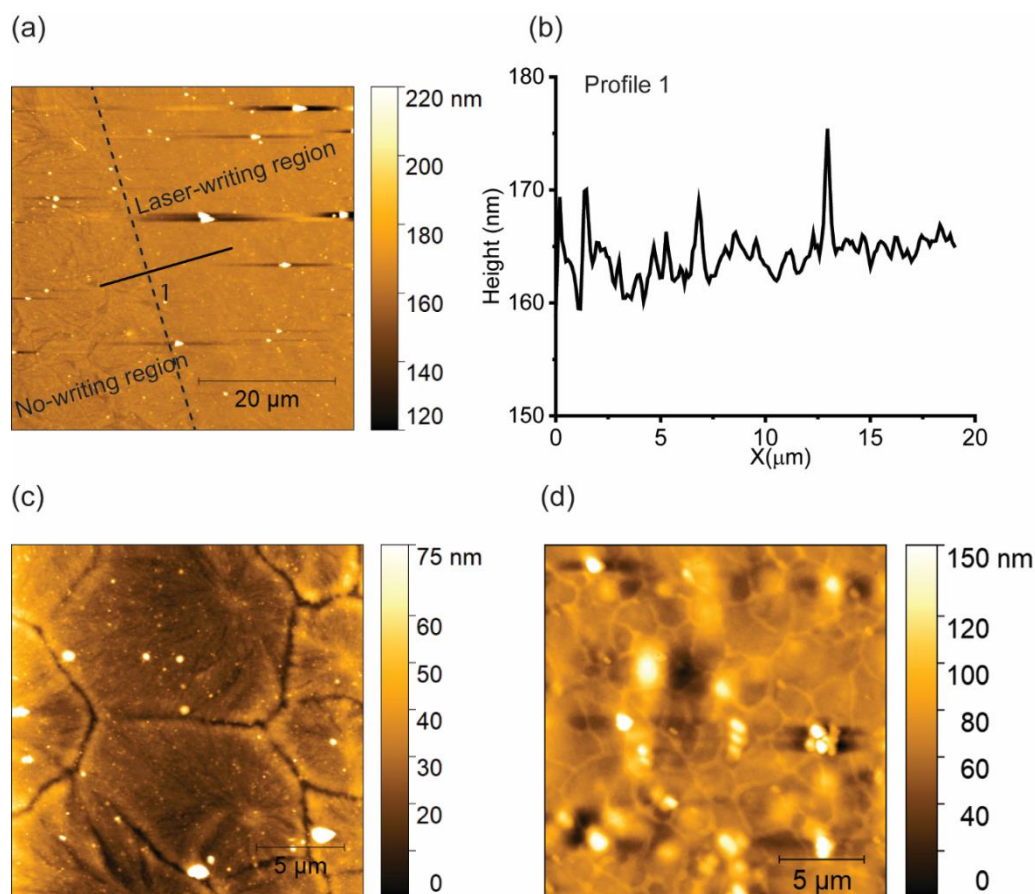


Figure S38. AFM characterization of film written at the optimized conditions: writing power is 8 mW and speed is 300 $\mu\text{m/s}$: (a) AFM of laser writing pattern including the laser-writing region, non-writing region and they are divided by the black dashed line, and (b) The height profile along the black line 1 in (a), suggesting the unchanged surface thickness; AFM images scanned in the (c) non-writing region and (d) laser-writing region.

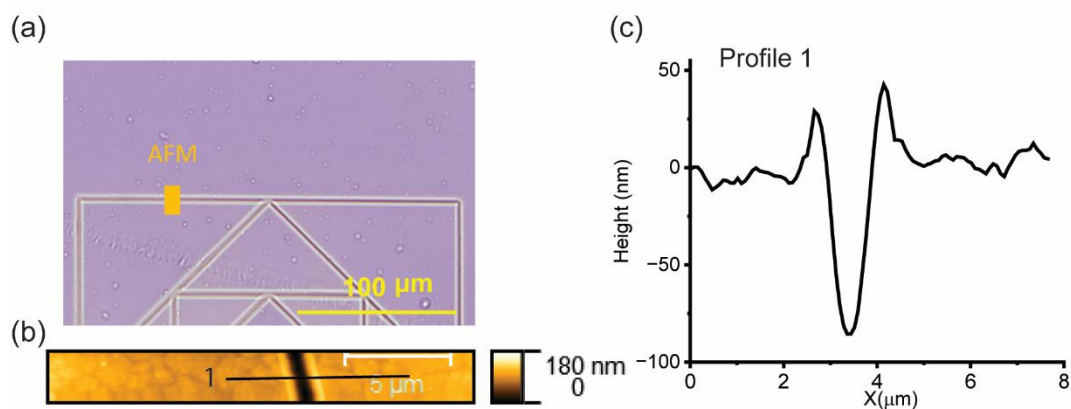


Figure S39. (a) Photo and (b) AFM of laser burned samples; the yellow region in the photo indicates where AFM probe scanned. (c) The height profile along the black line 1 in (b), indicating the obvious burning line.

References

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