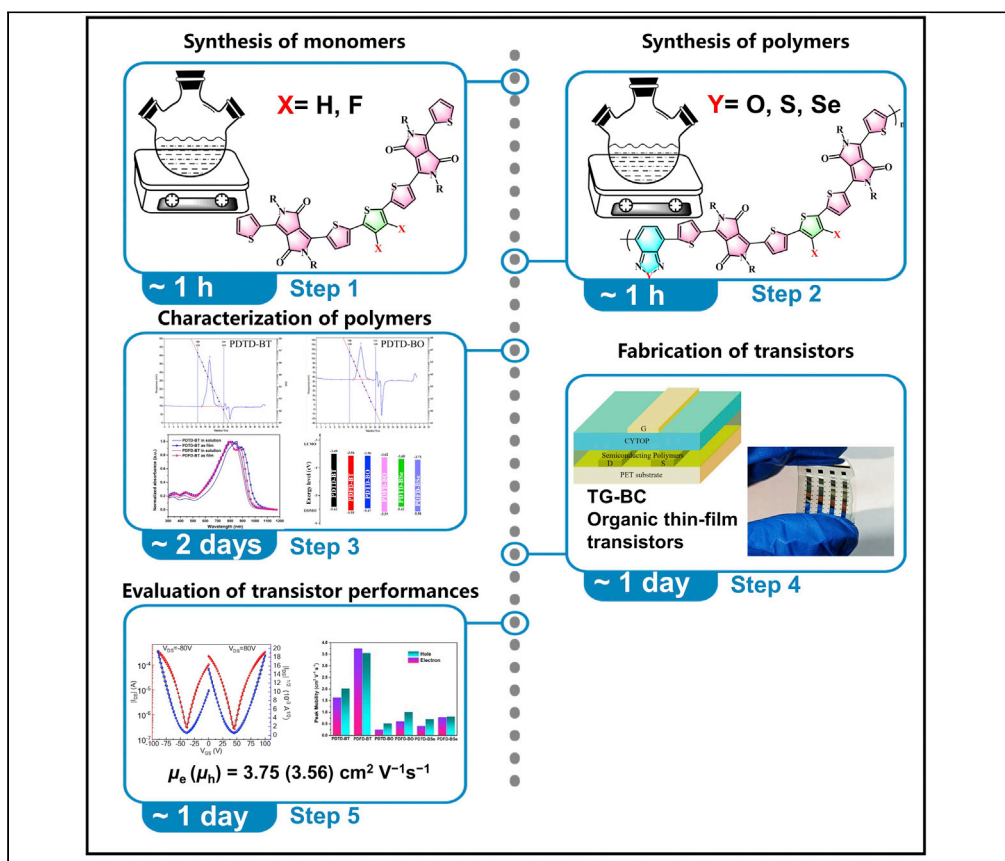


## Protocol

# Protocol for rapid synthesis of high-performance ambipolar semiconducting polymers using an all-C–H-activation strategy



Tao Shen, Wenhao Li, Yan Zhao, Yunqi Liu, Yang Wang  
yangwang@fudan.edu.cn

**Highlights**  
Synthesis of C–H reactive DPP-dimer type hydrogenated monomers

Rapid C–H activation polymerization of high-mobility ambipolar polymers

Characterization of high-mobility ambipolar polymers

Organic transistor performances of high-mobility ambipolar polymers

Syntheses using classic coupling reactions can be tedious, leading to a dearth of ambipolar semiconducting polymers. Here, we detail the rapid synthesis of balanced ambipolar polymers by using a carbon-hydrogen (C–H) activation strategy. Using this protocol, two C–H reactive hydrogenated monomers and six ambipolar polymers can be rapidly synthesized within 2 h via C–H activation and the optoelectronic properties of the resultant polymers can be characterized. We also describe the fabrication process and performance evaluation of the ambipolar polymers-based organic transistors.

Publisher's note: Undertaking any experimental protocol requires adherence to local institutional guidelines for laboratory safety and ethics.

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## Protocol

## Protocol for rapid synthesis of high-performance ambipolar semiconducting polymers using an all-C–H-activation strategy

Tao Shen,<sup>1</sup> Wenhao Li,<sup>1</sup> Yan Zhao,<sup>1</sup> Yunqi Liu,<sup>1,2</sup> and Yang Wang<sup>1,3,4,\*</sup><sup>1</sup>Laboratory of Molecular Materials and Devices, Department of Materials Science, Fudan University, 2005 Songhu Road, Shanghai 200438, China<sup>2</sup>Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry Chinese Academy of Sciences, Beijing 100190, China<sup>3</sup>Technical contact<sup>4</sup>Lead contact\*Correspondence: [yangwang@fudan.edu.cn](mailto:yangwang@fudan.edu.cn)  
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## SUMMARY

Syntheses using classic coupling reactions can be tedious, leading to a dearth of ambipolar semiconducting polymers. Here, we detail the rapid synthesis of balanced ambipolar polymers by using a carbon-hydrogen (C–H) activation strategy. Using this protocol, two C–H reactive hydrogenated monomers and six ambipolar polymers can be rapidly synthesized within 2 h via C–H activation and the optoelectronic properties of the resultant polymers can be characterized. We also describe the fabrication process and performance evaluation of the ambipolar polymers-based organic transistors.

For complete details on the use and execution of this protocol, please refer to Shen et al. (2022).

## BEFORE YOU BEGIN

Ambipolar semiconductor polymers that transport electrons and holes simultaneously are of great significance for the manufacture of cost-effective complementary metal oxide semiconductor (CMOS)-like circuits (Sirringhaus, 2014). Recently, diketopyrrolopyrrole (DPP)-based ambipolar semiconducting polymers have attracted much attention due to DPP's decent electron-withdrawing property, coplanar structure, and strong intermolecular interaction (Liu et al., 2020; Lee et al., 2012; Yang et al., 2017). However, several issues arise to restrain their practical use as ambipolar transporting materials. First of all, it is difficult to achieve well-balanced hole and electron mobility simultaneously. Upon copolymerization with donor units, such as oligothiophene, and thienothiophene, the resultant DPP-polymers usually display unbalanced ambipolar charge transport with predominant p-type properties (Li et al., 2011; Cinar and Ozturk, 2015). Secondly, the most unfavorable issue with the DPP-based polymers is related to their preparation by mostly Palladium-catalyzed Stille polymerization, which requires arduous purification of organo-stannanes as one of the comonomers (Carsten et al., 2011; Lee et al., 2018). Alternatively, C–H activation polymerization, the so-called direct arylation polymerization (DARp), which can construct conjugated polymers by using the direct activation of C–H bonds, appears as an environmentally benign and atom-economical protocol for semiconducting polymers (Facchetti et al., 2012; Segawa et al., 2015; Wang et al., 2019; Zhao et al., 2021). However, the successful example of DARp for high performance DPP-based ambipolar semiconducting polymers is only limited to the case that (*E*)-1,2-Bis(3,4-difluorothiophen-2-yl) ethene (4FTVT) is used as the hydrogenated comonomer unit (Gao et al., 2015). Furthermore, it requires 6 steps to prepare 4FTVT with very low total yield of 21%. With the above issues in present DPP-based polymers, it remains imperative and indispensable to rationally design polymer backbones for high and balanced ambipolar charge transport, as well as efficient synthesis and better



solution processability for printed organic electronics. Herein, we provide a detailed protocol for the rapid synthesis of high-performance balanced ambipolar DPP-based polymers by an all C-H activation strategy. The protocol only needs 2% of the reaction time that the traditional method costs and getting 4 times higher total yield compared to traditional method. This time-saving strategy brings a new platform for the efficient production of high-performance ambipolar semiconducting polymers and accordingly, opens the way to a wide range of applications in plastic electronics. Before one begins, the following preparations need to be carried out.

**Note:** All reagents were purchased from commercial suppliers and used without further purification.

### Preparation of reagent (for the synthesis of monomers)

⌚ Timing: 3 h

The starting compound 2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP) was prepared according to the literature (Ni et al., 2019) and the details are as follows.

#### 1. Synthesis of DPP.

- Add potassium carbonate ( $K_2CO_3$ ) (9.7 g, 70.0 mmol) and 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (7.0 g, 23.3 mmol) into a two-necked flask.
- Vacuum the flask and back-fill with  $N_2$ . Repeat three times.
- Add *N,N*-dimethylformamide (DMF) (150 mL) via syringe under  $N_2$ .
- Stir the reaction solution rigorously at 25°C for 5 min.
- Heat the reaction mixture to 120°C and keep stirring for 1 h.
- Add 2-octyldodecylbromide (25.3 g, 70.0 mmol) drop-wise via syringe under  $N_2$ .
- Stir the reaction mixture for another 2 h at 135°C.
- After cooling down to 25°C, pour the reaction mixture into water and extract with chloroform.
- Wash the combined organic layers with water three times, dry over sodium sulfate ( $Na_2SO_4$ ), and concentrate in vacuum by using rotary evaporation under vacuum (100 mbar) at 40°C.
- Purify the residue by column chromatography over silica gel using a mixture of petroleum ether (PE) and dichloromethane (DCM) as eluent (PE/DCM=5/1, v/v).
- After collecting all the products, remove the solvent by using rotary evaporation under vacuum (200 mbar) at 40°C.
- Recrystallize the product from methanol and dry under the vacuum to get the target compound as purple solid (yield 30%).
- Analyze the product by  $^1H$  NMR (400 MHz,  $CDCl_3$ ,  $\delta$ , ppm): 8.88 (d,  $J = 3.2$  Hz, 2H), 7.63 (d,  $J = 4.8$  Hz, 2H), 7.28 (t,  $J = 4.4$  Hz, 2H), 4.03 (d,  $J = 7.6$  Hz, 4H), 1.92, (br s, 2H), 1.31–1.22 (m, 64H), 0.90–0.85 (m, 12H).  $^{13}C$  (100 MHz,  $CDCl_3$ ,  $\delta$ , ppm): 161.9, 140.6, 135.3, 130.6, 130.0, 128.5, 108.1, 46.2, 37.7, 31.9, 31.8, 31.1, 30.0, 29.6, 29.54, 29.48, 29.34, 29.28, 26.2, 22.67, 22.65, 14.1. MALDI-TOF MS ( $m/z$ ):  $[M]^+$  calcd for  $C_{54}H_{88}N_2O_2S_2$ , 860.6; found, 861.1. Anal. calcd for  $C_{54}H_{88}N_2O_2S_2$ : C, 75.29; H, 10.30; N, 3.25; found: C, 75.31; H, 10.55; N, 3.18.

### KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
3,6-Di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione	Derthon Optoelectronic Materials Science Technology Co., Ltd.	CAS: 850583-75-4
2-Octyldodecylbromide	MAKKIN reagent	CAS: 69620-20-8

(Continued on next page)

<i>Continued</i>		
REAGENT or RESOURCE	SOURCE	IDENTIFIER
Sodium sulfate (Na <sub>2</sub> SO <sub>4</sub> )	Aladdin	CAS: 7757-82-6
Silica gel	Shanghai Titan Scientific Co., Ltd.	CAS: 63231-67-4
Potassium carbonate (K <sub>2</sub> CO <sub>3</sub> )	Aladdin	CAS: 584-08-7
<i>N,N</i> -Dimethylformamide (DMF) (anhydrous, 99.8%)	Sigma-Aldrich	CAS: 68-12-2
2,5-Dibromothiophene	Sigma-Aldrich	CAS: 3141-27-3
Cesium carbonate (Cs <sub>2</sub> CO <sub>3</sub> )	Sigma-Aldrich	CAS: 534-17-8
Pivalic acid (PivOH)	Sigma-Aldrich	CAS: 75-98-9
Tris(dibenzylideneacetone)dipalladium (Pd <sub>2</sub> (dba) <sub>3</sub> )	MAKIN reagent	CAS: 60748-47-2
Tris( <i>o</i> -methoxyphenyl) phosphine (P( <i>o</i> -anisyl) <sub>3</sub> )	Sigma-Aldrich	CAS: 4731-65-1
Toluene (99.0%)	Adamas	CAS: 108-88-3
Petroleum ether (PE)	Adamas	CAS: 8032-32-4
Dichloromethane (DCM)	Adamas	CAS: 75-09-2
Methanol	Adamas	CAS: 67-56-1
2,5-Dibromo-3,4-difluorothiophene	SunaTech Inc	CAS: 347838-15-7
<i>N,N</i> -Dimethylacetamide (DMAc)	Adamas	CAS: 127-19-5
4,7-Dibromo-2,1,3-benzothiadiazole	Derthon Optoelectronic Materials Science Technology Co., Ltd.	CAS: 15155-41-6
4,7-Dibromo-2,1,3-benzooxadiazole	Derthon Optoelectronic Materials Science Technology Co., Ltd.	CAS: 54286-63-4
4,7-Dibromo-2,1,3-benzoselenadiazole	Derthon Optoelectronic Materials Science Technology Co., Ltd.	CAS: 63224-42-0
Tetra- <i>n</i> -butylammonium hexafluorophosphate	Sigma-Aldrich	CAS: 3109-63-5
Acetonitrile	Sigma-Aldrich	CAS: 75-05-8
Acetone	Adamas	CAS: 67-64-1
Hexane	Adamas	CAS: 110-54-3
Chloroform	Adamas	CAS: 67-66-3
Deuterated chloroform	Sigma-Aldrich	CAS: 865-49-6
<i>Software and algorithms</i>		
ChemDraw Professional 18.0	PerkinElmer	<a href="https://www.perkinelmer.com/category/chemdraw">https://www.perkinelmer.com/category/chemdraw</a>
<i>Other</i>		
Nuclear Magnetic Resonance (NMR)	Varian Mercury Plus-400 spectrometer	NA
Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI–TO MS)	Bruker autoflex maX MALDI-TOF mass spectrometer	NA
Ultraviolet-Visible-near-IR Spectroscopy (UV-vis-NIR)	PerkinElmer Lambda 750 spectrophotometer	NA
Gel Permeation Chromatography (GPC)	GPC-PL220 high temperature GPC/SEC system	NA
Thermogravimetric Analysis (TGA)	METTLER STARe	NA
Cyclic Voltammetry (CV)	CHI760E voltammetric analyzer	NA

## MATERIALS AND EQUIPMENT

### Instruments (for structural characterization)

Technique	Condition
Nuclear Magnetic Resonance (NMR)	<sup>1</sup> H NMR (400 MHz) and <sup>13</sup> C NMR (100 MHz)
Gel Permeation Chromatography (GPC)	Use 1,2,4-trichlorobenzene as the eluent (150°C)
Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI–TOS MS)	Ion source: APCI Solvent: DCM
Combustion elemental analysis (Anal. Calcd)	Complete combustion at 1150°C under O <sub>2</sub> .

(Continued on next page)

**Continued**

Instruments (for structural characterization)

Technique	Condition
Thermogravimetric Analysis (TGA)	Set heating ramp of 10°C min <sup>-1</sup> , temperature from 25°C to 500°C under N <sub>2</sub> flow
Ultraviolet-Visible-near-IR Spectroscopy (UV-vis-NIR)	Use chloroform as the solvent for solution absorption measurement or spin-coating the polymer solution (5 mg/mL) on the glass substrate for the film absorption measurement. The measurement was done at 25°C. The wavelength is set from 300 to 1200 nm with a scan step of 1 nm.
Cyclic Voltammetry (CV)	0.1 M tetra- <i>n</i> -butylammonium hexafluorophosphate (nBu <sub>4</sub> NPF <sub>6</sub> ) in acetonitrile as electrolyte
Keithley S4200A semiconductor characterization	For p-type transistor transfer measurement, set V <sub>GS</sub> from -100 to 10 V, V <sub>DS</sub> = -80 V; For n-type transistor transfer measurement, set V <sub>GS</sub> from -10 to 120 V, V <sub>DS</sub> = 80 V. For p-type transistor out-put measurement, set V <sub>GS</sub> from -80 to 0 V, V <sub>G</sub> = 0–100 V with a step of 20 V; For n-type transistor transfer measurement, set V <sub>GS</sub> from 0 to 80 V, V <sub>G</sub> = 0–100 V with a step of 20 V. All the measurements were done in the glovebox filled with N <sub>2</sub> at 25°C.

**STEP-BY-STEP METHOD DETAILS**

**Synthesis of monomers**

⌚ Timing: 1 h

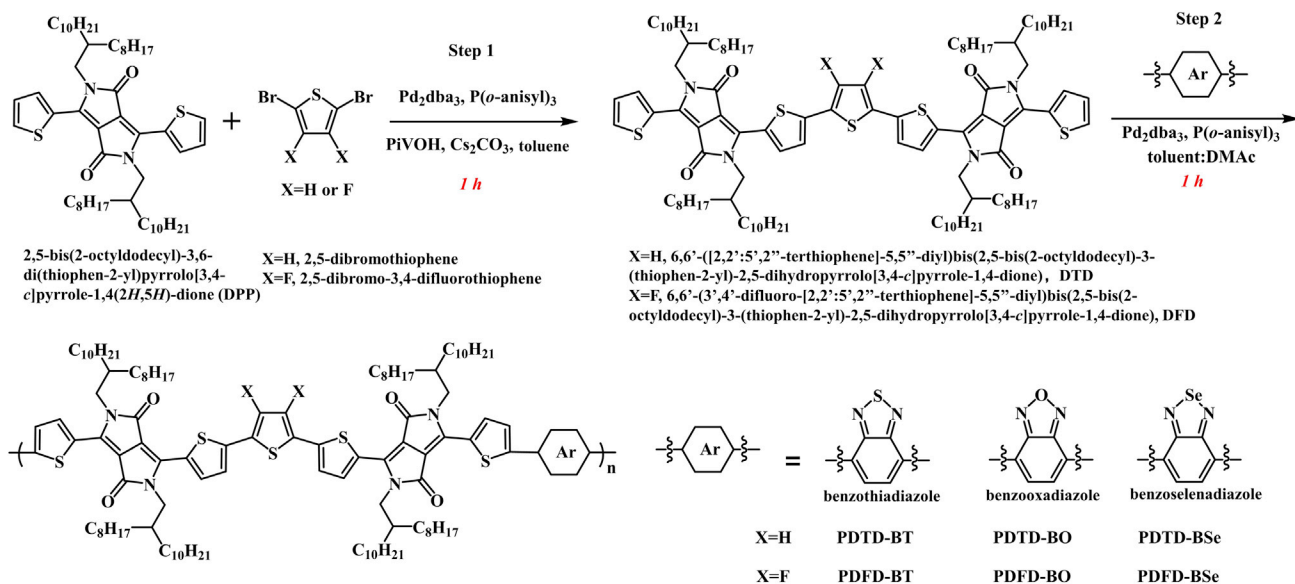
DPP-dimer type hydrogenated monomers, namely, 6,6'-([2,2':5',2''-terthiophene]-5,5''-diyl)bis(2,5--bis(2-octyldecyl)-3-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione) (DTD) and 6,6'-(3',4'-difluoro-[2,2':5',2''-terthiophene]-5,5''-diyl)bis(2,5-bis(2-octyldecyl)-3-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione) (DFD), were synthesized via C-H activation reactions as shown in [Scheme 1](#).

1. Synthesis of monomers (DTD, DFD).

- Add DPP (2.0 g, 2.3 mmol), 2,5-dibromothiophene (216.0 mg, 0.9 mmol) or 2,5-dibromo-3,4-difluorothiophene (250.0 mg, 0.9 mmol), anhydrous Cs<sub>2</sub>CO<sub>3</sub> (1.9 g, 5.8 mmol), PivOH (70.4 mg, 0.7 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (42.1 mg, 2 mol%), tris(*o*-methoxyphenyl) phosphine (31.3 mg, 4 mol%) successively into a Schlenk tube.
- Vacuum the tube and back-fill with N<sub>2</sub>. Repeat three times.
- Add anhydrous toluene (77 mL) via syringe.
- Stir the reaction mixture rigorously at 25°C for 5 min.
- Heat the reaction mixture to 110°C and keep stirring rigorously for 1 h under N<sub>2</sub> atmosphere.

⚠ **CRITICAL:** The reaction time should be controlled within 1 h to avoid the formation of oligomers.

- After cooling down to 25°C, remove the toluene by rotary evaporator under vacuum (50 mbar) at 50°C to afford the crude product.
- Purify the crude product by column chromatograph (CC) on silica gel using a mixture of PE and DCM as eluent (PE/DCM= 3/1, v/v).
- Collect the target product and remove the solvent by using rotary evaporation under vacuum (200 mbar) at 40°C.



**Scheme 1.** Synthetic route to the monomers and polymers

- Recrystallize the product from methanol and dry under the vacuum to get the target compound as purple-blue solid (yield 31%).
- Analyze the product by NMR and MALDI-TOF MS.

DTD:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.90 (m, 4H), 7.62 (s, 2H), 7.26 (m, 6H), 4.03 (s, 8H), 1.94 (s, 2H), 1.30–1.20 (m, 160H), 0.90–0.84 (m, 24H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 161.55, 161.44, 141.75, 141.05, 139.99, 139.09, 137.34, 136.99, 136.84, 135.67, 130.07, 128.52, 125.05, 108.40, 108.12, 46.41, 37.97, 30.30, 29.77, 22.93, 14.36. MALDI-TOF MS ( $M_w = 1802.95$ ): found  $m/z = 1803.06$  [M+].

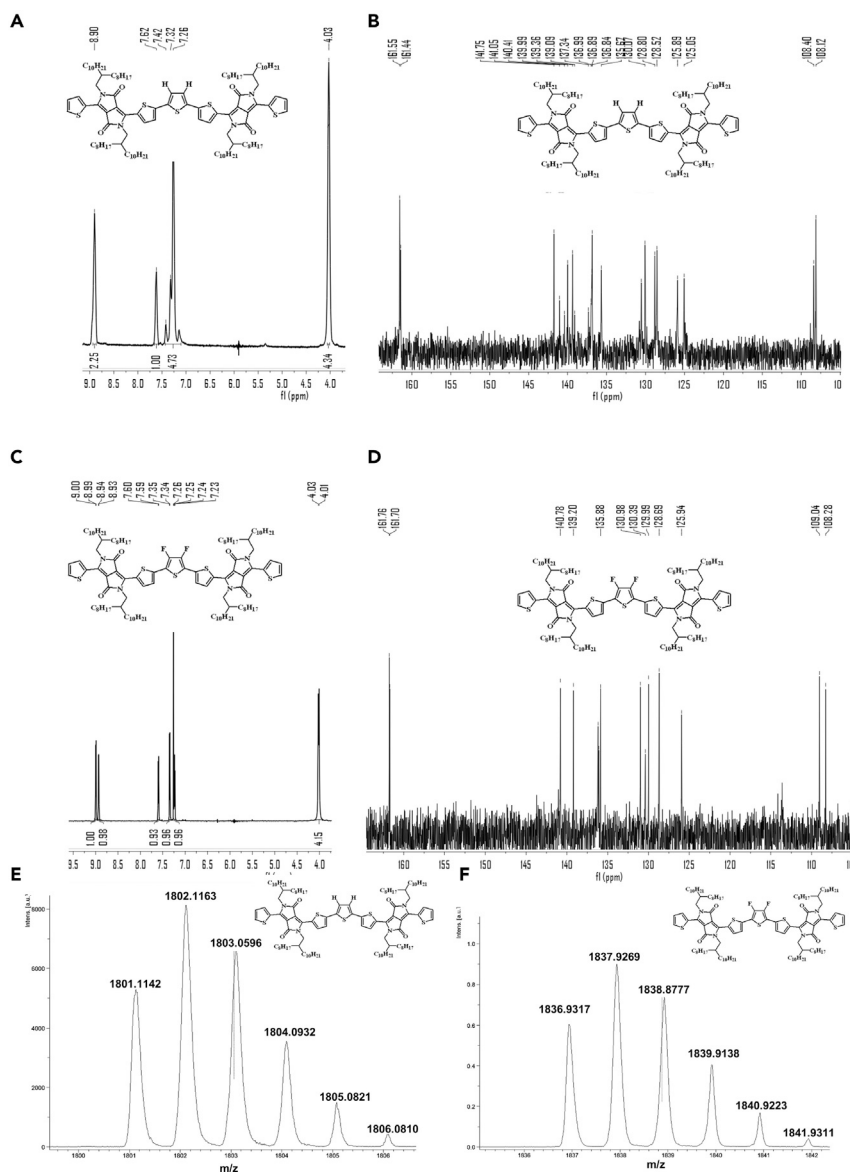
DFD:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 9.00 (d,  $J = 4$  Hz, 2H), 8.94 (d,  $J = 4$  Hz, 2H), 7.60 (d,  $J = 4$  Hz, 2H), 7.35 (d,  $J = 4$  Hz, 2H), 7.25 (t,  $J = 8$  Hz, 2H), 4.03 (d,  $J = 8$  Hz, 8H), 1.92 (s, 2H), 1.30–1.20 (m, 160H), 0.90–0.84 (m, 24H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 161.76, 161.70, 140.78, 139.20, 136.17, 136.08, 135.88, 130.98, 130.39, 129.99, 128.69, 125.94, 109.04, 108.28, 46.52, 38.35, 37.99, 32.16, 32.12, 31.52, 31.39, 30.31, 29.89, 29.81, 29.75, 29.55, 26.56, 22.92, 14.35. MALDI-TOF MS ( $M_w = 1838.93$ ): found  $m/z = 1838.88$  [M+]. The NMR and MALDI-TOF MS spectrum of DTD, DFD monomers are shown in Figure 1.

## Synthesis of polymers

⌚ Timing: 1 h

The obtained hydrogenated acceptor units (DTD, DFD) were directly coupled to the counter brominated acceptor units, such as dibromobenzothiadiazole (BT), dibromobenzoxadiazole (BO), and dibromobenzoselenadiazole (BSe) under the optimized DArP conditions, affording a series of acceptor-acceptor type copolymers, named PDTD-BT, PDTD-BO, PDTD-BSe, PDFD-BT, PDFD-BO, PDFD-BSe, shown in Scheme 1. For the detail of the optimization of DArP conditions, please refer to Shen et al. (2022).

2. Synthesis of polymers (Take PDTD-BT as an example).



**Figure 1. The NMR and MALDI-TOF MS spectrum of compounds DTD, DFD**

- (A)  $^1\text{H}$  NMR spectrum of compound DTD (400 M, r.t., in  $\text{CDCl}_3$ , displaying ppm range from 4 to 9).  
 (B)  $^{13}\text{C}$  NMR spectrum of compound DTD (100 M, r.t., in  $\text{CDCl}_3$ ).  
 (C)  $^1\text{H}$  NMR spectrum of compound DFD (400 M, r.t., in  $\text{CDCl}_3$ , displaying ppm range from 4 to 9).  
 (D)  $^{13}\text{C}$  NMR spectrum of compound DFD (100 M, r.t., in  $\text{CDCl}_3$ ).  
 (E) MALDI-TOF MS spectrum of compound DTD.  
 (F) MALDI-TOF MS spectrum of compound DFD.

- Add DTD (360 mg, 0.2 mmol), 4,7-dibromo-1,2,3-benzothiadiazole (58 mg, 0.2 mmol)  $\text{Pd}_2\text{dba}_3$  catalyst (9 mg, 5 mol %),  $\text{P}(o\text{-anisyl})_3$  (7 mg, 10 mol%), PivOH (20 mg, 0.2 mmol), and  $\text{K}_2\text{CO}_3$  (80 mg, 0.6 mmol) successively into a Schlenk tube.
- Vacuum the tube and back-fill with  $\text{N}_2$ . Repeat three times.
- Add a mixed anhydrous DMAc/toluene solvent (1 mL+1 mL) via syringe.
- Stir the reaction at  $25^\circ\text{C}$  under  $\text{N}_2$  for 5 min with rotating speed of 800 rpm.
- Heat the reaction mixture to  $120^\circ\text{C}$  and keep stirring for 1 h under  $\text{N}_2$ .
- After cooling down to  $25^\circ\text{C}$ , pour the reaction mixture into chilled methanol (100 mL).

- g. Collect the crude product by filtration.
- h. Purify the crude product by using Soxhlet extraction with methanol, acetone, hexane, and chloroform.
- i. Collect the chloroform fraction and concentrate by removing most of solvent with rotary evaporator under vacuum (100 mbar) at 35°C.
- j. Precipitate the concentrated polymer solution into chilled methanol (100 mL).
- k. Collect the solid by filtration and dry under vacuum to afford the target polymer as black solid.
- l. Analyze the polymers by combustion elemental analysis (Anal. Calcd), <sup>1</sup>H NMR, and high-temperature GPC.

PDTD-BT: A dark solid (yield 89%) was obtained. Anal. calcd for C<sub>118</sub>H<sub>178</sub>N<sub>6</sub>O<sub>4</sub>S<sub>6</sub> (%): C, 73.16; N, 4.34; S, 9.93. Found (%): C, 72.54; N, 4.34; S, 9.42. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm) : 8.91–8.80 (br), 8.69–8.64 (br), 7.95–7.70 (br), 7.27–7.20 (br), 7.17–6.99 (br), 4.06–3.93 (br), 2.09–1.94 (br), 1.37–1.16 (br), 0.80–0.70 (br) M<sub>n</sub> = 25.4 kDa, PDI = 2.9.

PDTD-BO: A dark solid (yield 88%) was obtained. Anal. calcd for C<sub>118</sub>H<sub>178</sub>N<sub>6</sub>O<sub>5</sub>S<sub>5</sub> (%): C, 73.78; N, 4.37; S, 8.35. Found (%): C, 73.36; N, 4.47; S, 8.21. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm) : 8.90–8.80 (br), 8.69–8.65 (br), 8.12–7.92 (br), 7.68–7.54 (br), 7.18–7.00 (br), 4.05–3.90 (br), 2.00–1.90 (br), 1.36–1.16 (br), 0.80–0.70 (br) M<sub>n</sub> = 29.5 kDa, PDI = 2.9.

PDTD-BSe: A dark solid (yield 78%) was obtained. Anal. calcd for C<sub>118</sub>H<sub>178</sub>N<sub>6</sub>O<sub>4</sub>S<sub>5</sub>Se (%): C, 71.43; N, 4.24; S, 8.08. Found (%): C, 71.35; N, 4.28; S, 8.04. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm) : 8.91–8.74 (br), 8.69–8.64 (br), 8.08–7.88 (br), 7.60–7.50 (br), 7.27–7.17 (br), 4.06–3.93 (br), 1.98–1.90 (br), 1.35–1.16 (br), 0.80–0.70 (br) M<sub>n</sub> = 11.8 kDa, PDI = 2.5.

PDFD-BT: A dark solid (yield 86%) was obtained. Anal. calcd for C<sub>118</sub>H<sub>176</sub>F<sub>2</sub>N<sub>6</sub>O<sub>4</sub>S<sub>6</sub> (%): C, 71.83; N, 4.26; S, 9.75. Found (%): C, 71.19; N, 4.14; S, 9.43. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm) : 9.06–8.94 (br), 8.70–8.60 (br), 7.94–7.71 (br), 7.18–7.09 (br), 4.06–3.90 (br), 1.98–1.90 (br), 1.35–1.16 (br), 0.80–0.70 (br) M<sub>n</sub> = 20.2 kDa, PDI = 1.9.

PDFD-BO: A dark solid (yield 84%) was obtained. Anal. calcd for C<sub>118</sub>H<sub>176</sub>F<sub>2</sub>N<sub>6</sub>O<sub>5</sub>S<sub>5</sub> (%): C, 72.42; N, 4.29; S, 8.19. Found (%): C, 72.45; N, 4.38; S, 8.12. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm) : 9.03–8.84 (br), 8.70–8.60 (br), 7.94–7.81 (br), 7.40–7.30 (br), 7.18–7.10 (br), 4.06–3.90 (br), 1.98–1.90 (br), 1.35–1.16 (br), 0.80–0.70 (br) M<sub>n</sub> = 23.7 kDa, PDI = 2.5.

PDFD-BSe: A dark solid (yield 78%) was obtained. Anal. calcd for C<sub>118</sub>H<sub>176</sub>F<sub>2</sub>N<sub>6</sub>O<sub>4</sub>S<sub>5</sub>Se (%): C, 70.16; N, 4.16; S, 7.94. Found (%): C, 69.41; N, 4.06; S, 7.76. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm) : 8.95–8.87 (br), 8.85–8.80 (br), 8.76–8.68 (br), 7.95–7.85 (br), 7.56–7.35 (br), 7.19–7.10 (br), 4.00–3.90 (br), 1.95–1.85 (br), 1.35–1.16 (br), 0.80–0.70 (br) M<sub>n</sub> = 12.3 kDa, PDI = 2.3.

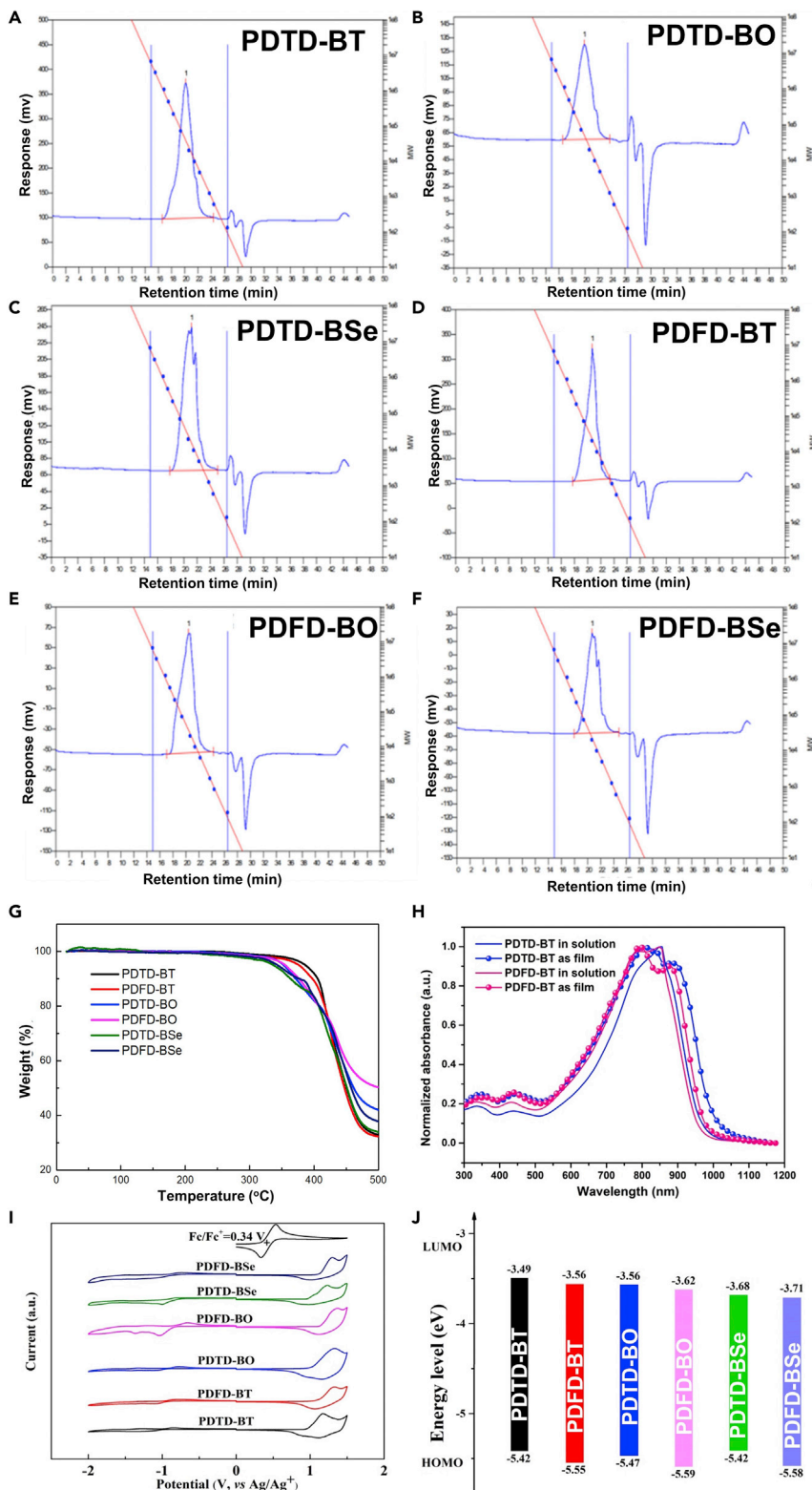
### Characterization of molar masses, optical and electrochemical properties of the polymers

⌚ Timing: 2 days

High-temperature Gel Permeation Chromatography (HT-GPC) analysis, ultraviolet-vis-near infrared (UV-vis-NIR), and cyclic voltammetry (CV) were employed to characterize the properties of polymers.

3. Use HT-GPC to characterize the molecular weight (M<sub>n</sub>) and polydispersity index (PDI) of the polymers. Use polystyrene as the standard and 1, 2, 4-trichlorobenzene (TCB) as eluent under 150°C (Figures 2A–2F). The data are listed in the session of Synthesis of polymers (vide supra).
4. Use thermogravimetric Analysis (TGA) to characterize the thermal stability of the polymers, with a heating ramp of 10°C min<sup>-1</sup>. Figure 2G shows all polymers have 5% weight loss temperature (defined as degradation temperature, T<sub>d</sub>) higher than 300°C.





## Figure 2. Characterization of molar masses, thermal, optical, and electrochemical properties of the ambipolar polymers

(A–F) GPC curves for the six polymers of (A) PDTD-BT; (B) PDTD-BO; (C) PDTD-BSe; (D) PDFD-BT; (E) PDFD-BO; (F) PDFD-BSe; (G) TGA curves of the six polymers. (H) UV–vis–NIR absorption spectra of PDTD-BT and PDFD-BT in dilute solution and thin film.

(I) CV of the six polymer films.

(J) HOMO/LUMO energy levels diagram of the six polymers. Figures 2H–2J reprinted with permission from Shen et al. (2022).

5. Use the UV-vis-NIR to investigate the photophysical properties of the polymers in chloroform and thin films. Figure 2H shows the UV–vis–NIR absorption spectra of PDTD-BT and PDFD-BT in dilute  $\text{CHCl}_3$  solution and as thin-film state.
6. Use CV to characterize the frontier molecular orbital energies of the polymers, i.e., the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels.
  - a. Prepare 0.1 M tetra-*n*-butylammonium hexafluorophosphate ( $n\text{Bu}_4\text{NPF}_6$ ) in acetonitrile as the supporting electrolyte.
  - b. Purge the supporting electrolyte solution thoroughly with argon before all CV measurements.
  - c. Use a platinum disk as the working electrode, a Pt wire as the counter electrode, and a Ag/AgCl as the reference electrode.
  - d. Drop the polymer films from chloroform solutions onto a Pt working electrode (2 mm in diameter).
  - e. Measure the redox potential of the polymers from -2 to 0 V and 0–1.5 V under the scanning rate of 0.1 V/s (Figure 2I).
  - f. Measure the redox potential of ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) from 0 to 1.5 V under the scanning rate of 0.1 V/s for calibration. Other conditions were the same (it was located at 0.34 V vs. the Ag/AgCl electrode, Figure 2I).
  - g. Calculate the HOMO and LUMO energy levels according to the following equations (Figure 2J):

$$E_{\text{HOMO}} = -(\varphi_{\text{ox}} + 4.46)(\text{eV}) \quad (\text{Equation 1})$$

$$E_{\text{LUMO}} = -(\varphi_{\text{re}} + 4.46)(\text{eV}) \quad (\text{Equation 2})$$

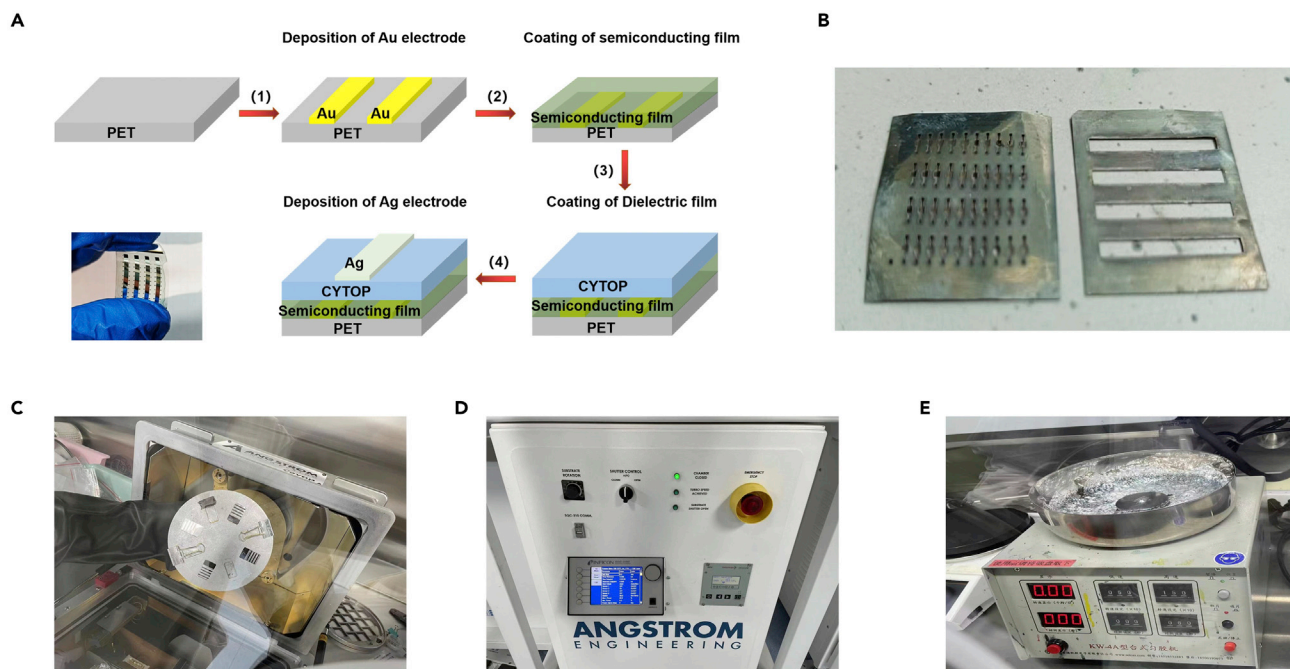
where  $\varphi_{\text{ox}}$  is the onset oxidation potential vs. Ag/AgCl and  $\varphi_{\text{re}}$  is the onset reduction potential vs. Ag/AgCl.

## Fabrication of the ambipolar polymers-based transistors

⌚ Timing: 1 day

Flexible top-gate/bottom-contact (TG-BC) organic thin-film transistors based on six polymers were fabricated. All the spin-coating and testing processes were done in the in the glove box with  $\text{N}_2$  atmosphere. The content of  $\text{H}_2\text{O}$  and  $\text{O}_2$  in the glove box were below 0.1 ppm.

7. Fabrication of transistors.
  - a. Pattern the source and drain electrodes (3 nm Cr and 30 nm Au) on PET substrate by standard thermal evaporation process, as shown in Figure 3A step 1. Figure 3B shows the photograph of the masks of source-drain and gate electrodes used in this protocol. Figure 3C shows the carrier to load the masks during the thermal evaporation. Figure 3D shows the thermal evaporation system.
  - b. Spin-coat the semiconductor layer from chlorobenzene solution ( $5 \text{ mg mL}^{-1}$ ), then anneal at  $160^\circ\text{C}$  for 30 min followed by cooling down process, as shown in Figure 3A step 2. Figure 3E shows the spin-coating machine used in this protocol.



**Figure 3. Fabrication of the ambipolar polymers-based organic thin-film transistors**

- (A) Scheme of preparation process of transistors.  
 (B) Photograph of the masks of source-drain and gate electrodes.  
 (C) Photograph of the carrier to load the masks during the thermal evaporation.  
 (D) Photograph of the thermal evaporation system.  
 (E) Photograph of the spin-coating machine.

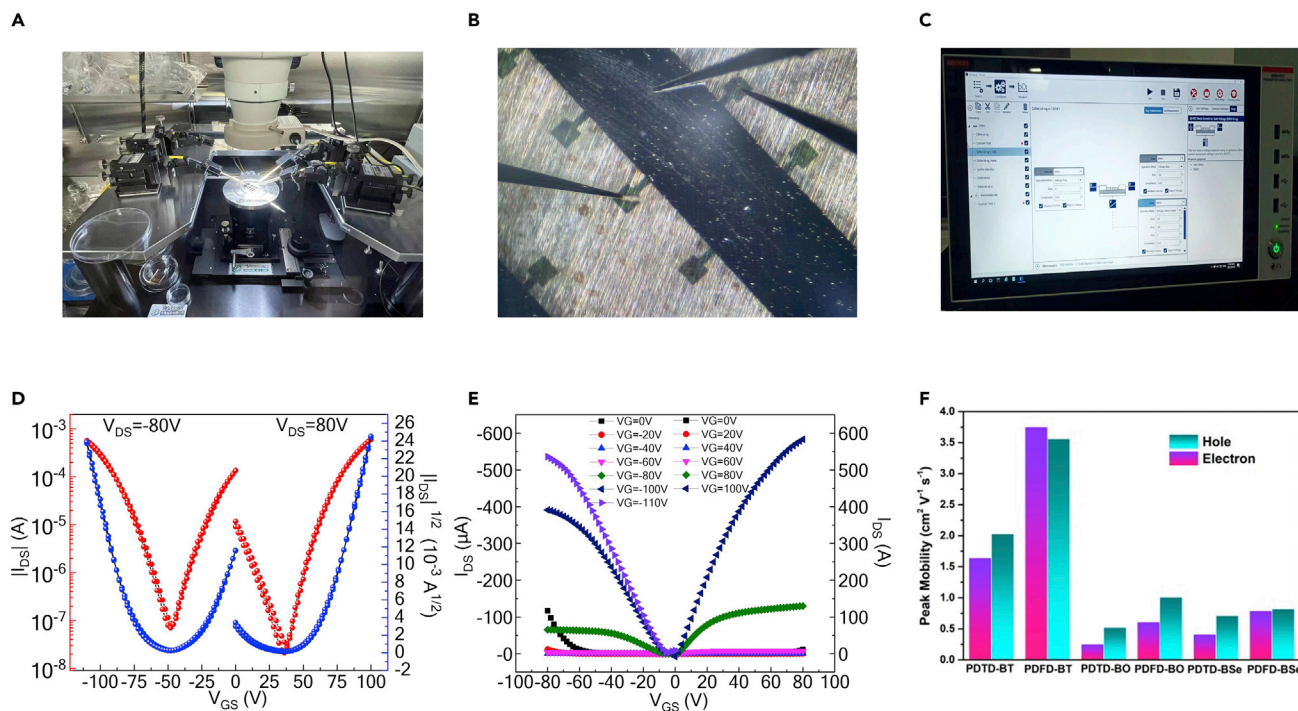
- c. Spin-coat the dielectric layer from diluted CYTOP solutions (CTL-809M: CT-SOLV180 = 3:1 volume ratio, Asahi Glass Co., Ltd.), then anneal at 120°C for 30 min, as shown in [Figure 3A](#) step 3.
- d. Evaporate 80 nm Ag as the gate electrode on top under high vacuum ( $< 10^{-6}$  Torr) to complete the transistor fabrication, as shown in [Figure 3A](#) step 4.

### Evaluation of transistor performance

Ⓞ Timing: 1 day

The performances of the organic thin-film transistors based on six polymers were tested by using Keithley 4200A semiconductor characterization system. All the operation was done in the  $N_2$  atmosphere.

8. Evaluate the transistor performances.
  - a. Put the device on the probe station. [Figure 4A](#) shows the probe station.
  - b. Contact the corresponding three probes with the S-D and gate electrodes of the transistors, as shown in [Figure 4B](#).
  - c. Evaluate the device performances with Keithley S4200A semiconductor characterization system, as shown in [Figure 4C](#).
  - d. Calculate the average slope of the  $|I_{SD}|^{1/2}$  vs  $V_g$  plot in the  $V_g = -80$  to  $-100$  V for p-type characteristics and  $V_g = 80$ – $120$  V region for n-type characteristics. [Figures 4D](#) and [4E](#) show the transfer and output curves of PDFD-BT transistor, respectively.
  - e. Calculate the mobilities according to the following equation:



**Figure 4. Evaluation of the transistor performance**

(A) Photograph of the probe station.

(B) Photograph of the probes, S-D and gate electrodes.

(C) Photograph of the Keithley 4200A semiconductor characterization system.

(D) Transfer curves of PDFD-BT-based transistors.

(E) Output curves of PDFD-BT-based transistors.

(F) The hole and electron mobility comparison profile of the polymers. Figures 4D–4F reprinted with permission from Shen et al. (2022).

$$I_{SD} = (W/2L)C_i\mu(V_g - V_{th})^2 \quad (\text{Equation 3})$$

where  $I_{SD}$  is the drain current in the saturated regime,  $W$  (4,200  $\mu\text{m}$ ) and  $L$  (50  $\mu\text{m}$ ) are the semiconductor channel width and length, respectively,  $C_i$  ( $C_i = 2.7 \text{ nF cm}^{-2}$ ) is the capacitance per unit area of the CYTOP dielectric layer, and  $V_g$  and  $V_{th}$  are the gate voltage and threshold voltage, respectively. Figure 4F shows the hole and electron mobility comparison profile of all the polymers.

## EXPECTED OUTCOMES

This protocol allows for the rapid synthesis of high-performance well-balanced ambipolar polymers via an all-C-H activation strategy. First, we rapidly synthesized 2 hydrogenated acceptor-dimer type monomers via C-H activation reactions within 1 h. Second, we rapidly synthesized 6 ambipolar polymers by copolymerizing the above 2 monomers with other 3 dibromo-comonomers within 1 h. After that, we characterized the properties and fabricated the organic transistors based on these ambipolar polymers. Compared with the reported C-H activation method (Ni et al., 2019), this protocol possesses large difference and advancement. From the point view of the chemical structures, the acceptor-acceptor backbone strategy, heteroatom substitution and fluorine substitution were both employed (Scheme 1). Thanks to the synergistic effect of the above molecular design strategies, it resulted in the high and ideally balanced hole and electron mobilities up to 3.56 and 3.75  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ , respectively, which is among the best performance of balanced ambipolar polymers. Most importantly, our protocol only took 1 h to prepare monomers and another 1 h to afford high-mobility ambipolar polymers. Therefore, one of the highlights of our work is the large reduction of the reaction time. The all-C-H-activation strategy presented here only needs 2% of the reaction

time that the traditional method takes, and the total yield is 4 times higher than that of the traditional method.

### LIMITATIONS

There are several limitations to this protocol. First, the molecular weights of PDTD-BSe and PDFD-BSe polymers are relatively low, due to the coordination of Se atom to the center of palladium catalyst, which may inhibit the polymerization (Meena et al., 2020). Second, during the fabrication of transistors, all the operation should be done in the N<sub>2</sub> atmosphere, due to the poor air stability of polymers.

### TROUBLESHOOTING

#### Problem 1

Low yields of DTD and DFD monomers (synthesis of monomers).

#### Potential solution

The moderate yields of DTD are due to the formation of oligomers. Because of the highly reactive nature of DTD, we believe that DTD can continue to react with dibromothiophene, leading to other byproducts. Therefore, the reaction time should be controlled within 1 h.

#### Problem 2

Insoluble materials in CHCl<sub>3</sub> (synthesis of polymers).

#### Potential solution

Because of the highly reactive nature of DTD, the time for DArP should be controlled within 1 h.

#### Problem 3 (synthesis of polymers)

The polymerization is sensitive to the ratio of toluene and DMAc in the mixed solvent. A slight change of the ratio may lead to a largely different polymerization rate.

#### Potential solution

The volume of the solvent should be measured carefully and appropriately to reduce the operative error. For example, if the monomers (0.2 mmol each) with mixed solvent (2 mL, toluene:DMAc= 1:1) are used for polymerization, it will be easier for the experiment operator to measure the volume of the solvent.

#### Problem 4

Poor stability of the organic thin film transistors (fabrication of the ambipolar polymers-based transistors).

#### Potential solution

During the fabrication of transistors, all the operation should be done in the N<sub>2</sub> atmosphere, including the performance evaluation.

### RESOURCE AVAILABILITY

#### Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Yang Wang (yangwang@fudan.edu.cn).

#### Materials availability

The reagents generated in this study will be available from the lead contact upon request.

### Data and code availability

NMR spectra have been deposited at Mendeley Data: <https://doi.org/10.17632/4p97kf9ydf.1>. All other data reported in this paper will be shared by the lead contact upon request. This paper does not report original code.

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### AUTHOR CONTRIBUTIONS

Y.W. developed the concept and designed the experiments; T.S. synthesized the monomers and polymers and characterized the properties of polymers. W.L. and Y.Z. fabricated and evaluated the devices; T.S. and Y.W. wrote the manuscript. All the authors discussed the results. Y.W. and Y.L. supervised the whole project administration.

### DECLARATION OF INTERESTS

The authors declare no competing interests.

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