Supplementary Information

High-Performance n-Type Stretchable OFETs Enabled by Molecular Engineering of Flexible Polymers

Qian Che,^{†ab} Tianhao Zhang,^{†c} Weifeng Zhang,^{*ab} Jiadi Chen,^{ac} Yunchao Zhang,^c Zhihui Chen,^a Youjia Li,^c Lei Yang,^c Liping Wang, ^{*c} and Gui Yu ^{*ab}

1. Materials

All the starting materials, reagents, and catalysts are purchased from Acros, Sigma-Aldrich, or other commercial sources and directly used without any further purification unless otherwise explained. The monomer azo-BDOPV was synthesized according to our previous work.¹

2. Synthetic Methods of Monomers and Polymers

1,2-bis(5-bromothiophen-2-yl)ethane-1,2-dione (M1). To a 250 ml three neck roundbottom flask (RBF) protected by inert atmosphere, aluminum chloride (1.59 g, 12 mmol), anhydrous dichloromethane (20 ml) and a stir bar were added. Subsequently, the system was cooled down to 0°C and stirred for 10 minutes. Then, the mixture of 2bromothiophene (3.91 g, 24 mmol) and oxalyl dichloride (1.52 g, 12 mmol) were added dropwise in the RBF by additional funnel. After finished, the system was allowed to stir at room temperature overnight. The mixture was poured into dilute cold hydrochloric acid to quench the reaction, then extracted by dichloromethane in three times. The organic phase was dried by anhydrous sodium sulfate. The solvents were removed by rotary evaporator and the crude product was further purified by recrystallization in ethanol to afford M1 as orange solid (3.24g, 71%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.89 (s, 2H), 7.18 (s, 2H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 179.38, 137.77, 131.70, 128.12. HR-MS calcd. for C₁₀H₄Br₂O₂S₂: 380.07136 Found: 380.33031.

1,4-bis(5-bromothiophen-2-yl)butane-1,4-dione (M2). The compound M2 was

^a Beijing National Laboratory for Molecular Sciences, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of

Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China. E-mail: <u>yugui@iccas.ac.cn</u>; zhangwf@iccas.ac.cn

^{b.} School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 100049, P. R. China

^c School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, P. R. China. E-mail: lpwang@mater.ustb.edu.cn

obtained from 2-bromothiophene (3.91 g, 24 mmol) and succinyl dichloride (1.86 g, 12 mmol) by the same procedure as used to prepare M1. The final product of M2 was tangerine soild (3.62 g, 74%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.54 (s, 2H), 7.12 (s, 2H), 3.30 (s, 4H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 190.17, 145.03, 132.28, 131.32, 122.90, 32.41. HR-MS calcd. for C₁₂H₈Br₂O₂S₂: 408.12472. Found: 407.83030.

1,6-bis(5-bromothiophen-2-yl)hexane-1,6-dione (M3). The compound M3 was obtained from 2-bromothiophene (3.91 g, 24 mmol) and adipoyl dichloride (2.20 g, 12 mmol) by the same procedure as used to prepare M1. The final product of M3 was yellow soild (4.08 g, 78%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.43 (d, 2H), 7.09 (d, 2H), 2.87 (s, 4H), 1.80 (s, 4H). HR-MS calcd. For C₁₄H₁₂Br₂O₂S₂: 436.17808. Found: 436.4992.

P1. To a schlenk flask, monomer aza-BDOPV (155.7 mg, 0.09 mmol, 0.9 e.q.), compound M1 (3.8 mg, 0.01 mmol, 0.1 e.q.), (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (52.8 mg, 0.1 mmol, 1 e.q.), $Pd_2(dba)_3$ (1.5 mg), P(o-tol)_3 (4.5 mg), and chlorobenzene (5 mL) were added successively. The system was charged with argon and through a thee-pump-thaw cycle for three times. The tube was heated to 115°C for 48 h. After finished, the mixture was allowed to cool down to room temperature and poured into dilute hydrochloric acid and methanol to quench the reaction. The crude soild was afforded by fliteration and further purified by Soxhlet extraction, using methanol, acetone, and n-hexane successively. o-dichlorobenzene was used as the final extraction solvent to acquire **P1** (197.4 mg, 93%). Anal. Calcd. for $C_{513}H_{768}F_{10}N_{18}O_{28}S_{11}$:C, 75.34; H, 9.47; N, 3.08; S, 4.31. Found: C, 72.85; H, 9.26; N, 2.93; S, 3.81.

P2. The polymer **P2** was obtained from monomer aza-BDOPV (155.7 mg, 0.09 mmol, 0.9 e.q.), compound M2 (4.1 mg, 0.01 mmol, 0.1 e.q.), (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (52.8 mg, 0.1 mmol, 1 e.q.) by the same procedure as used to prepare **P2**. Yield: 91% (193.4 mg). Anal. Calcd. for $C_{514}H_{770}F_{10}N_{18}O_{28}S_{11}$:C, 75.36; H, 9.47; N, 3.08; S, 4.30. Found: C, 73.90; H, 9.28; N,

2.94; S, 4.46.

P3. The polymer **P3** was obtained from monomer aza-BDOPV (155.7 mg, 0.09 mmol, 0.9 e.q.), compound M3 (4.4 mg, 0.01 mmol, 0.1 e.q.), (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (52.8 mg, 0.1 mmol, 1 e.q.) by the same procedure as used to prepare **P3.** Yield: 95% (202.2 mg). Anal. Calcd. for $C_{515}H_{772}F_{10}N_{18}O_{28}S_{11}$:C, 75.37; H, 9.48; N, 3.07; S, 4.30. Found: C, 73.98; H, 9.34; N, 2.97; S, 4.28.

3. General Measurements

¹H nuclear magnetic resonance (NMR) and ¹³C NMR spectra are tested on a Bruker AVANCE 300 machine, using deuterated chloroform (CDCl₃) as deuterated reagent. High resolution mass spectra (HRMS) were recorded on a Shimadzu QP 2010 gas chromatograph mass spectrometer, and high-resolution matrix assisted laser desorption/ionization time-of-flight mass spectra (HR-MALDI-TOF) were performed on a 9.4T Solarix FT-ICR mass spectrometer. Elemental analyses were carried out by using a CARLO ERBA 1106 Elemental Analyser. The number-average molecular weight (M_n) , weight-average molecular weight (M_w) , and polydispersity index (PDI) of copolymers were acquired by using an Agilent Technologies PL-GPC220 series Gel permeation chromatography (GPC) with 1,2,4-trichlorobenzene (TCB) as eluent at 150°C, and using narrow-polydispersity polystyrene standards to calibrate. Thermogravimetric analyses (TGA) were tested on a DTG-60 instrument under nitrogen flow, heating from 50°C to 550 °C with a heating rate of 20°C min⁻¹. The differential scanning calorimetry (DSC) tests were conducted by DSC2-00881 (172.23.188.10) instrument, circulating from 50°C to 250°C with a heating/cooling rate of 10°C min⁻¹. Ultraviolet-Visible-NearInfrared (UV-Vis-NIR) absorption spectra were acquired by UH5700 Spectrophotometer. The ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES) was examined by Axis-Nova CJ109, Kratos. Cyclic voltammetric (CV) measurements were tested on a CHI660C electrochemistry workstation with a scan rate of 50 mV s⁻¹. The atomic force

microscope (AFM) images were acquired on a Digital Instruments Nanoscope V atomic force microscope, which operated in tapping mode. The grazing incidence wide angle X-ray scattering (GIWAXS) data were obtained by illuminating the thin film samples at a constant incidence angle of 0.2° at beamline BL02U2 of the Shanghai Synchrotron Radiation Facility (SSRF).

4. Device Fabrication and Characterization

The PDMS prepolymer mixture (with a PDMS to curing agent ratio of 10:1) was slowly coated onto a glass slide, then placed in a vacuum oven and heated at 80°C for 3h to ensure complete curing. After being completely peeled off from the glass slide, it was used as the substrate. Gold with a thickness of 50 nm was thermal evaporated onto the PDMS substrate through a shadow mask to serve as the source/drain electrodes, and the substrate and electrodes were treated with ultraviolet/ozone (UVO) for 20 min. The glass slides were washed with secondary water, ethanol, and acetone by ultrasonic cleaning sequentially, placed in Petri dishes, modified with octadecyltrichlorosilane (OTS), and heated in a vacuum oven at 120 °C for 3 h, then cooled down to room temperature to obtain OTS hydrophobic-treated glass slides. A 60 mg/mL PVA/H2O was spin-coated onto the OTS-modified glass slide at 1000 rpm for 60 s, followed by annealing in a vacuum at 100°C for 30 minutes. Subsequently, polymer solutions (with o-DCB solutions of P1-P3 all at a concentration of 4.0 mg/mL) were spin-coated at 1500 rpm for 60 s and then thermally annealed at 140°C for 20 min. The PVA/polymer composite film was then transferred onto the PDMS substrate with gold source/drain electrodes and heated in a vacuum oven at 80°C for 30 min, followed by cooling to room temperature to improve interlayer contact. Finally, the prepared device was placed on a 100°C hot plate, and a spray gun loaded with 2 mL of AgNWs solution was used to uniformly spray the gate electrode onto the PDMS covered with a shadow mask. All the devices were measured by using a Keithley 4200 semiconductor parameter analyzer. The charge carrier mobility was calculated from the saturation regime according to the following equation:

$$I_{DS} = \left(\frac{W}{2L}\right) C_i \mu (V_G - V_T)^2$$

Where I_{DS} denotes the saturation drain current, W/L is the ratio of the channel width and channel length, C_i is the capacitance per unit area of the gate dielectric layer, and V_G and V_T are the gate voltage and threshold voltage, respectively.



5. Figures and Tables

Figure S1. GPC distribution plots of the polymers (a) P1, (b) P2, (c) P3.



Figure S2. TGA traces of the polymers P1, P2 and P3.



Figure S3. DSC curves of the polymers P1, P2 and P3.



Figure S4. cyclic voltammetry diagrams of the polymers P1, P2, and P3.



Figure S5. (a, b, c, d) Typical transfer and (e, f, g, h) output characteristics of **P1**-based stretchable OFETs in the initial state and at different strains (15%, 30%, 50%), with charge transfer parallel to the strain direction.



Figure S6. (a, b, c, d) Typical transfer and (e, f, g, h) output characteristics of **P1**-based stretchable OFETs in the initial state and at different strains (15%, 30%, 50%), with charge transfer perpendicular to the strain direction.



Figure S7. (a, b, c, d) Typical transfer and (e, f, g, h) output characteristics of **P2**-based stretchable OFETs in the initial state and at different strains (15%, 30%, 50%), with charge transfer parallel to the strain direction.



Figure S8. (a, b, c, d) Typical transfer and (e, f, g, h) output characteristics of **P2**-based stretchable OFETs in the initial state and at different strains (15%, 30%, 50%), with charge transfer perpendicular to the strain direction.



Figure S9. (a, b, c, d) Typical transfer and (e, f, g, h) output characteristics of **P3**-based stretchable OFETs in the initial state and at different strains (15%, 30%, 50%), with charge transfer parallel to the strain direction.



Figure S10. (a, b, c, d) Typical transfer and (e, f, g, h) output characteristics of **P3**based stretchable OFETs in the initial state and at different strains (15%, 30%, 50%), with charge transfer perpendicular to the strain direction.



Figure S11. (a, b, c) Typical transfer and (e, f, g) output characteristics of **P1** (a, d), **P2** (b, e), and **P3** (c, f)-based stretchable OFETs after 500 stretching cycles at 30% strain, with charge transfer parallel to the strain direction.



Figure S12. (a, b, c) Typical transfer and (e, f, g) output characteristics of P1 (a, d), P2

(b, e), and **P3** (c, f)-based stretchable OFETs after 500 stretching cycles at 30% strain, with charge transfer perpendicular to the strain direction.

Polymer	Substrate	μ_0 [cm ² V ⁻¹ s ⁻¹]	$\frac{Strain/\mu_l}{[\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}]}$	Reference
N2200	PDMS	0.44	50%/0.22	2
N2200	PDMS	0.18	50%/0.07	3
C12-DPP	SEBS	0.463	100%/0.1	4
DPPT-TT+SEBS	SEBS	0.288	100%/0.183	5
DPP-TT+[6]CPP	PDMS	0.85	100%/0.15	6
PPT-4	PDMS	0.2	100%/0.1	7
P1	PDMS	0.44	50%/0.20	This work
P2	PDMS	0.34	50%/0.17	This work
P3	PDMS	0.52	50%/0.29	This work

Table S1. Performance comparison of the intrinsically stretchable OFETs

6. References

- K. Shi, W. Zhang, D. Gao, S. Zhang, Z. Lin, Y. Zou, L. Wang and G. Yu, *Adv. Mater.*, 2018, **30**, 1705286.
- 2 H. Shim, K. Sim, B. Wang, Y. Zhang, S. Patel, S. Jang, T. J. Marks, A. Facchetti and C. Yu, *Nat. Electron.*, 2023, **6**, 349.
- 3 H. Shim, F. Ershad, S. Patel, Y. Zhang, B. Wang, Z. Chen, T. J. Marks, A. Facchetti and C. Yu, *Nat. Electron.*, 2022, 5, 660.
- J. Mun, G.-J. N. Wang, J. Y. Oh, T. Katsumata, F. L. Lee, J. Kang, H.-C. Wu, F. Lissel, S. Rondeau-Gagne', J. B.-H. Tok and Z. Bao, *Adv. Funct. Mater.*, 2018, 28, 1804222.
- 5 M. H. Kim, M. W. Jeong, J. S. Kim, T. U. Nam, N. T. P. Vo, L. Jin, T. I. Lee and J. Y. Oh, *Sci. Adv.*, 2022, 8, eade2988.
- J. Mun, J. Kang, Y. Zheng, S. Luo, H.-C. Wu, N. Matsuhisa, J. Xu, G.-J. N. Wang,
 Y. Yun, G. Xue, J. B.-H. Tok and Z. Bao, *Adv. Mater.*, 2019, **31**, 1903912.

7 J. Chen, M. Zhu, M. Shao, W. Shi, J. Yang, J. Kuang, C. Wang, W. Gao, C. Zhu,
 R. Meng, Z. Yang, Z. Shao, Z. Zhao, Y. Guo and Y. Liu, *Adv. Mater.*, 2023, 36, 2305987.

7. ¹H NMR and ¹³C NMR spectra



Figure S13. ¹H NMR and ¹³C NMR spectra of compound M1.



Figure S14. ¹H NMR and ¹³C NMR spectra of compound M2.



Figure S15. ¹H NMR and ¹³C NMR spectra of compound M3.