Supporting Information

Naphthalenediimide-Based Copolymers Incorporating Vinyl-Linkages for High-Performance Ambipolar Field-Effect Transistors and Complementary-Like Inverters under Air

Huajie Chen,[□] Yunlong Guo,[□] Zupan Mao,[□] Gui Yu,^{*} Jianyao Huang, Yan Zhao, and Yunqi Liu*

Synthetic Procedures and Characterization

Materials: All starting materials were purchased from Aldrich or Alfar Aesar, and used directly without further purification. *N,N'*-bis(2-octyldodecyl)-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide) (**M1**)^[1], and *N,N'*-bis(2-decyltetradecyl)-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide) (**M2**)^[2], 1,2-(*E*)-bis(5'-trimethylstannayl-2'-*C*-thienyl)ethane (**M3**)^[3] 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (**M4**)^[4] were prepared according to the literature procedures.

General Procedures for Stille Polymerization and Polymer Purification.

Synthesis of PNVt-8: To a 50 mL air-free Schlenk flask was added 1,2-(*E*)-bis(5-(trimethylstannanyl)-2-(*C*-thienyl)ethene (93 mg, 0.18 mmol), *N,N'*-bis(2-octyldodecyl)-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide) (**M1**) (178 mg, 0.18 mmol), Pd₂(dba)₃ (9 mg), P(*o*-tol)₃ (24.6 mg), and dry toluene (5 mL) under nitrogen atmosphere. The flask was subjected to a freeze-pump-thaw cycle for three times. The mixture was then stirred for 4 days at 115 °C. After cooling down to room temperature, the resultant mixture was added to

24 200 mL of methanol containing 15 mL of concentrate hydrochloric acid and then stirred for 6 h. The
 25 crude product was collected by filtration and washed with methanol (100 mL), acetone (100 mL),
 26 and hexane (100 mL), respectively. The crude polymer was further purified by Soxhlet extraction
 27 with methanol for 6 h, acetone for 6 h, hexane for 6 h, and finally chloroform for 12 h. A deep blue
 28 solid was obtained after removing chloroform (174 mg, 95.0% yield). GPC: $M_n = 24.3$ KDa, $M_w =$
 29 64.1 KDa, PDI = 2.64. Elemental analysis (%) Calcd. for $(C_{64}H_{92}N_2O_4S_2)_n$: C, 75.54; H, 9.11; N,
 30 2.75; Found: C, 75.69; H, 8.89; N, 2.87.

MW Averages
 Mp: 50365 Mn: 24301 Mv: 56975 Mw: 64061
 Mz: 129320 Mz+1: 217649 PD: 2.6361

Figure S1. ^1H NMR (top) spectra of PNVT-8 in CDCl_3 . High temperature GPC (bottom) analysis of a PNVT-8 sample used in this study.

Synthesis of PNVT-10: The synthesis of **PNVT-10** is similar as described above. For **PNVT-10**: (reaction solvent: 5 mL of toluene; reaction time: 4 days; reaction temperature: 115 °C). A deep blue solid was obtained after removing the solvent (189 mg, 93% yield). GPC: $M_n = 23.7$ KDa, $M_w = 58.4$ KDa, PDI = 2.46. Elemental analysis (%) Calcd: for $(\text{C}_{72}\text{H}_{108}\text{N}_2\text{O}_4\text{S}_2)_n$: C, 76.54; H, 9.64; N, 2.48; Found: C, 76.49; H, 9.56; N, 2.53.

MW Averages

Mp: 48695 Mn: 23671 Mv: 52414 Mw: 58396
Mz: 112539 Mz+1: 187024 PD: 2.4670

Distribution Plots

Figure S2. ¹H NMR (top) spectra of PNVT-10 in CDCl₃. High temperature GPC (bottom) analysis of a PNVT-10 sample used in this study.

Synthesis of P(NDI2OD-T2): The synthesis of **P(NDI2OD-T2)** is similar as described above. For **P(NDI2OD-T2)**: (reaction solvent: 5 mL of toluene; reaction time: 4 days; reaction temperature: 115 °C). A deep blue solid was obtained after removing the solvent (170 mg, 95% yield). GPC: M_n = 18.8 KDa, M_w = 43.4 KDa, PDI = 2.31. Elemental analysis (%) Calcd: for (C₆₂H₉₀N₂O₄S₂)_n: C, 75.10; H, 9.15; N, 2.83; Found: C, 74.89; H, 9.18; N, 2.78.

Figure S3. ^1H NMR (top) spectra of P(NDI2OD-T2) in CDCl_3 . High temperature GPC (bottom) analysis of a P(NDI2OD-T2) sample used in this study.

Figure S4. TGA (a) and DSC (b) plots of the NDI-based copolymers measured under N_2 atmosphere (Heating and cooling rates are $10\text{ }^\circ\text{C min}^{-1}$).

65 **Figure S5.** Optimized molecular structures and HOMO/LUMO orbits calculated by B3LYP 6-31G*
 66 of the methyl-substituted NDI-TVT and NDI-T2 trimers.

Table S1. The Mobility of the BGBC FET devices based on the NDI-based polymers with different channel lengths.

Channel length	40 μm		50 μm	
Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	P	N	P	N
P(NDI2OD-T2)	NA	0.19	NA	0.18
P(NDI2OD-T2)-PFBT	NA	0.26	NA	0.28
PNVT-8	0.15	0.78	0.11	0.65
PNVT-8-PFBT	0.02	1.15	0.04	1.4
PNVT-10	0.13	0.55	0.12	0.50
PNVT-10-PFBT	0.02	1.13	0.03	0.95

Table S2. Fundamental parameters of TGBC OFET devices based on the NDI-based polymers measured under 20~40% air humidity

Polymer	Time	<i>n</i> -channel			<i>p</i> -channel		
		μ_e [cm ² V ⁻¹ s ⁻¹]	V_{th} [V]	I_{on}/I_{off}	μ_h [cm ² V ⁻¹ s ⁻¹]	V_{th} [V]	I_{on}/I_{off}
PNVT-8	0 day	1.07 (±0.22)	71	>10 ⁴	0.13 (±0.03)	-51	>10 ⁴
	3 days	1.04 (±0.15)	74	>10 ⁴	0.13 (±0.02)	-55	>10 ⁴
	10 days	1.07 (±0.13)	72	>10 ⁴	0.12 (±0.02)	-54	>10 ³
	15 days	0.97 (±0.11)	70	>10 ⁴	0.10 (±0.02)	-59	>10 ³
	21 days	0.73 (±0.12)	70	>10 ⁴	0.10 (±0.02)	-61	>10 ³
	25 days	0.53 (±0.11)	76	>10 ⁴	0.08 (±0.01)	-52	>10 ³
	30 days	0.56 (±0.08)	79	>10 ⁴	0.06 (±0.01)	-54	>10 ³
PNVT-10	0 day	1.05 (±0.30)	50	>10 ⁴	0.21 (±0.03)	-60	>10 ⁴
	3 days	1.15 (±0.26)	55	>10 ⁴	0.20 (±0.02)	-58	>10 ⁴
	10 days	1.28 (±0.25)	61	>10 ⁴	0.16 (±0.02)	-48	>10 ³
	15 days	1.17 (±0.23)	61	>10 ⁴	0.15 (±0.02)	-49	>10 ³
	21 days	1.13 (±0.21)	68	>10 ⁴	0.14 (±0.01)	-42	>10 ³
	25 days	1.06 (±0.18)	65	>10 ⁴	0.13 (±0.01)	-50	>10 ³
	30 days	1.00 (±0.15)	64	>10 ⁴	0.10 (±0.01)	-50	>10 ³

Figure S6. Typical transfer (a) and output (b) curves of the P(NDI2OD-T2) based BGBC FET devices with $W = 1400 \mu\text{m}$ and $L = 50 \mu\text{m}$, exhibiting an electron mobility of $0.19 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Au electrodes were modified by PFBT, typical transfer (c) and output (d) curves of the P(NDI2OD-T2) based BGBC FET devices with $W = 1400 \mu\text{m}$ and $L = 40 \mu\text{m}$, affording an electron mobility of 0.27

cm² V⁻¹ s⁻¹; Typical transfer (e) and output (f) curves of the P(NDI2OD-T2) based TGBC FET devices with $W = 8800 \mu\text{m}$ and $L = 80 \mu\text{m}$, affording an electron mobility of $0.34 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Figure S7. Typical transfer (a) and output (b) curves of the PNVT-10 based BGBC FETs with $W = 1400 \mu\text{m}$ and $L = 40 \mu\text{m}$, exhibiting a hole mobility of $0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an electron mobility of $0.55 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; Au electrodes were modified by PFBT, Typical transfer (c) and output (d) curves of

the PNVT-10 based BGBC FETs with $W = 1400 \mu\text{m}$ and $L = 50 \mu\text{m}$, affording a hole mobility of $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an electron mobility of $0.85 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; Typical transfer (e) and output (f) curves of the PNVT-10 based TGBC FETs with $W = 8800 \mu\text{m}$ and $L = 80 \mu\text{m}$, exhibiting a hole mobility of $0.30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an electron mobility of $1.57 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Figure S8. The I-V characteristics of hysteresis tests for TGBC FET devices based on PNVT-8: (a) output curves and (b) transfer curves for *p*-type transport; (c) output curves and (d) transfer curves for *n*-type transport.

111

112

113

Figure S9. The plot of current on/off cycles for the PNVT-8 based TGBC FETs.

114

115

116

117

Figure S10. Typical transfer curves and gain of a complementary-like inverter based on PNVT-8.

119 After 2 months in laboratory air (20~40% air humidity), PNVT-8 based inverter still kept a high gain

120 of 45.

121

122

123 **Reference**

- 124 [1] a) Chen, Z. H.; Zheng, Y.; Yan, H.; Facchetti, A. *J. Am. Chem. Soc.*, **2009**, *131*, 8; b) Huang, H.;
125 Chen, Z. H.; Ortiz, R. P.; Newman, C.; Usta, H.; Lou, S.; Youn, J.; Noh, Y. Y.; Baeg, K. J.;
126 Chen, L. X.; Facchetti, A. *J. Am. Chem. Soc.*, **2012**, *134*, 10966.
- 127 [2] Zhou, W. Y.; Wen, Y. G.; Ma, L. C.; Liu, Y. Q.; Zhan, X. W. *Macromolecules*, **2012**, *45*, 4115.
- 128 [3] Chen, H. J.; Guo, Y. L.; Gui, Y.; Zhao, Y.; Zhang, J.; Gao, D.; Liu H. T.; Liu, Y. Q. *Adv. Mater.*,
129 **2012**, *24*, 4618.
- 130 [4] McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; MacDonald, I.; Shkunov, M.; Sparrowe,
131 D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabinyc, M. L.; Kline, R. J.; McGehee, M. D.; Toney,
132 M. F. *Nat. Mater.*, **2006**, *5*, 328.
- 133