Electronic supplementary information (ESI)

The effect of bridging groups on charge transport properties of 5-benzothiophene substituted anthracenes

Xiaosong Shi,[ab#] Yanan Sun,[ab#] Jie Liu,*[a] Yicai Dong,[a] Yanjun Shi,*[ac] Yuanping Yi,[a] and Lang Jiang*[ab]

[a] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.
[b] University of the Chinese Academy of Sciences, Beijing 100049, China.
[c] Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, China.
[#] These authors contributed equally to this work.
*Correspondence: liujie2009@iccas.ac.cn, shiyanjun@cczu.edu.cn, ljiang@iccas.ac.cn

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Section S1. Materials Synthesis and Characterization

All reagents were used as received from commercial resources unless otherwise specified.

Material Synthesis

M5-1

To a 250 mL flask charged with a magnetic bar, 5/6- bromobenzo[b]thiophene (10 mmol), bis(pinacolato)diboron (20 mmol), Pd(OAc)2 (0.5 mmol), S-phos (1 mmol), KOAc (30 mmol) were added under argon. Then 100 mL degassed DMF was added, and the whole system was heated at 80 $^\circ$C for 20 h. Then the mixture was poured into water, extracted with ethyl acetate (50 mL×3), and separated. The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. Further purification by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (4 : 1) as eluent afforded the product as a white solid (2.39 g, 92% yield).

^{1}H NMR (300 MHz, CDCl3) δ (ppm): 7.90 (d, 1H), 7.52 (s, 1H),7.44 (d, 1H), 7.33 (d, 1H), 6.23 (d, 1H), 1.33 (s, 12H). MS (EI) m/z: 260 (M$^+$).

M5-0

To a 100 mL flask charged with a magnetic bar, 5- bromobenzo[b]thiophene (10 mmol), CuI (0.6 mmol) Pd(PPh$_3$)$_2$Cl$_2$ (0.3 mmol) were added under argon. Then 20 mL ethanolamine, 30 mL THF, and 2 mL 2-methylbut-3-yn-2-ol were added. The whole system was warmed up to 80°C and kept for 8 h. After cooling down to room temperature, the organic solvent was removed under vacuum. Then 50 mL water was added, and the extracted with dichloromethane (30 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. Further purification by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (1:1) as eluent afforded the product as a white solid (1.95 g, 90% yield). M5-0:

^{1}H NMR (300 MHz, Chloroform-d) δ 7.95 (d, J = 1.7 Hz, 1H), 7.73 (d, J = 8.3 Hz, 1H), 7.47 (d, J = 5.5 Hz, 1H), 7.40 (dd, J = 8.3, 1.5 Hz, 1H), 7.30 (d, J = 5.4 Hz, 1H), 2.31 (s, 1H), 1.65 (s, 6H). MS (EI) m/z: 216 (M$^+$).

M5-3

To a 50 mL flask charged with a magnetic bar, M5-0 (5 mmol), and NaOH (25 mmol) were added under argon, then 15 mL anhydrous toluene was added, and the whole system was refluxed

at 110 °C for 1h, then the solvent was vacuum evaporated. Further purification by column chromatography on silica gel using petroleum ether as eluent gives M5-3 as a white needle-like solid (0.75 g, 95%yield). The two compounds were used directly for the next reaction.

M5-2

In a 100 mL flask charged with a magnetic bar, a mixture of bis(pinacolato)diboron (6.6 mmol), Sodium methoxide (1.2 mmol), triphenylphosphine (0.36 mmol), CuBr (0.3 mmol), and 30 mL THF was added under argon, the mixture was stirred for 30 min at room temperature. To the mixture, M5-3 (6 mmol) and methanol (12 mL) were added. The mixture was stirred at room temperature for another 8 h. Then the solvent was removed under vacuum, and further purification by column chromatography on silica gel using petroleum ether: dichloromethane (4:1) as eluent giving M5-2 as white solid (1.46 g, 85%).

^{1}H NMR (300 MHz, Chloroform-d) δ 7.90 – 7.79 (m, 2H), 7.58 – 7.46 (m, 2H), 7.44 (d, J = 5.4 Hz, 1H), 7.33 (d, J = 5.5 Hz, 1H), 6.23 (d, J = 18.4 Hz, 1H), 1.33 (s, 12H). MS (EI) m/z: 286 (M$^+$).

5-BTA

To a 50 mL flask charged with a magnetic bar, M5-1 (1 mmol), 2-bromoanthracene (1 mmol), and Pd(PPh$_3$)$_4$ (0.05 mmol) were added under argon. Then 10 mL toluene 2 mL ethanol and 2M K$_2$CO$_3$ 2 mL were added. The whole system was refluxed overnight. The crude product was obtained by filtration. And the filtrate was further purified by gradient sublimation, obtaining the final product as a yellow crystalline powder (~220 mg, 70%).

^{1}H NMR (300 MHz, Chloroform-d) δ 8.48 (d, J = 11.0 Hz, 2H), 8.24 (d, J = 16.4 Hz, 2H), 8.12 (d, J = 8.8 Hz, 1H), 8.02 (dd, J = 8.6, 5.1 Hz, 3H), 7.81 (ddd, J = 15.1, 8.6, 2.0 Hz, 2H), 7.53 – 7.42 (m, 5H). MS (EI) m/z: 310 (M$^+$). Calculated for C22H14S (%): C: 85.12, H: 4.55. Found: C: 85.16, H: 4.54.

5-BTVA

Similar to the synthesis of 5-BTA, obtaining yellow crystalline powder (230 mg，70%).

The ^{1}H NMR was not obtained because of its poor solubility.

MS (EI) m/z: 336 (M$^+$). Calculated for C24H16S (%): C: 85.68, H: 4.79. Found: C: 85.56, H: 4.79.

5-BTEA

To a 50 mL flask charged with a magnetic bar, M5-3 (1mmol), 2-bromoanthracene (1 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.03 mmol), CuI (0.06 mmol) were added under argon, then 10 mL THF and 2 mL Et3N was added, the mixture was stirred at reflux overnight, then filtrated. The filtrate was further

purified by gradient sublimation, obtaining the final product as a yellow crystalline powder (~216 mg, 65%).

^{1}H NMR (300 MHz, Chloroform-d) δ 8.41 (s, 2H), 8.25 (s, 1H), 8.08 (s, 1H), 7.99 (d, J = 9.0 Hz, 3H), 7.88 (d, J = 8.3 Hz, 1H), 7.52 (dd, J = 23.1, 7.7 Hz, 5H), 7.36 (d, J = 5.5 Hz, 1H). MS (EI) m/z: 334 (M$^+$). Calculated for C24H14S (%): C: 86.19, H: 4.22. Found: C: 86.03, H: 4.21.

Nuclear Magnetic Resonance

^{1}H NMR was recorded using a Bruker Advance 300 MHz Spectrometer. ^{1}H NMR spectra were referenced to CDCl$_3$ (7.26 ppm).

Elemental analysis

Elemental analysis was carried out by Flash EA 1112.

Section S2. Materials physicochemical characterization

Photophysical studies of solution sample

UV-vis absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer in a 1 cm quartz cell for solution samples. And 1×10^{-5} M THF solution was used for monomers measurements.

Electrochemical analysis

Cyclic voltammetry measurements were performed in 0.1 M electrolyte solution (Bu4NPF6) in CH_2Cl_2 with a sample concentration of 10^{-3} M at room temperature in N_2 atmosphere, using a Pt disk as a working electrode, Ag/AgCl as a reference electrode, and Pt wire as an auxiliary electrode. Ferrocene was added to the analyzed solution at the end of the measurement as an internal reference.

Thermal gravimetric analysis (TGA)

TGA was performed on an STA 409 PC thermogravimeter under an N_2 flow at a heating rate of 10ºC min^{-1}.

Table S1. Summary of absorption and emission characters and calculated band gaps, orbital energy levels, and decomposition temperatures

Compound	5-BTA	5-BTVA	5-BTEA
E_g (eV)	3.06	2.91	3.04
HOMO (eV)	5.61	5.30	5.67
LUMO (eV)	2.55	2.39	2.63
$T_{95\%\text{-dec}}$ (ºC)	282.1	**320.8**	294.0

Section S3. Single-crystal structures

X-ray crystal structure analysis

High-quality single crystals of three compounds were grown from saturated THF solution at room temperature for X-ray analysis. X-ray diffraction intensity data were collected on a Rigaku Synergy-R (Japan) with confocal monochromator Mo K\α radiation (Table S1).
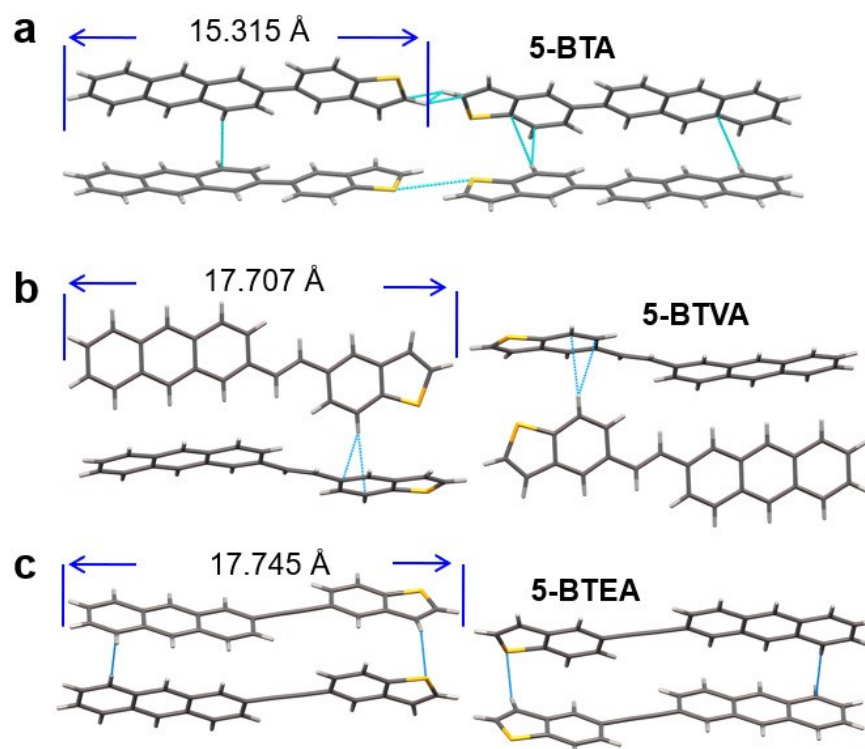
Figure S1 Typical head-head out-of-plane stacking of three asymmetric molecules. (a) **5-BTA**, (b) **5-BTVA,** and (c) **5-BTEA**.

Table S1. Crystal data and structure refinement for three compounds.

| Compound	5-BTA (CCDC: 2282393)	5-BTVA (CCDC: 2282397)	5-BTEA (CCDC: 2282398)
Empirical formula	$C_{22}H_{14}S$	$C_{48}H_{32}S_2$	$C_{24}H_{14}S$
Formula weight	310.39	672.85	334.41
Temperature/K	169.99(10)	169.99(13)	169.98(10)
Crystal system	triclinic	triclinic	monoclinic
Space group	P-1	P-1	$P2_1/c$
Unit cell dimensions	a = 5.96810(10) Å	a = 5.93870(10) Å	a = 37.0770(6) Å
	b = 7.52570(10) Å	b = 7.39720(10) Å	b = 5.84810(10) Å
	c = 32.8655(3) Å	c = 36.9135(8) Å	c = 7.49050(10) Å
	α = 86.5170(10)°	α = 94.4240(10)°	α = 90°
	β = 85.9290(10)°	β = 93.435(2)°	β = 94.2530(10)°
	γ= 89.8220(10)°	γ= 90.2300(10)°	γ= 90°
Volume/Å³	1469.68(3)	1613.80(5)	1619.69(4)
Z	4	2	4
ρ_{calc}g/cm³	1.403	1.385	1.371
μ/mm^{-1}	1.893	1.769	1.762
F(000)	648.0	704.0	696.0
Crystal size/mm³	0.156 × 0.132 × 0.123	0.3 × 0.21 × 0.05	0.125 × 0.112 × 0.025
2Θ range for data collection/°	5.402 to 151.044	4.81 to 150.816	4.78 to 150.532
Index ranges	-7 ≤ h ≤ 7	-7 ≤ h ≤ 7	-45 ≤ h ≤ 34
	-9 ≤ k ≤ 9	-8 ≤ k ≤ 9	-6 ≤ k ≤ 6
	-40 ≤ l ≤ 39	-46 ≤ l ≤ 42	-9 ≤ l ≤ 9
Reflections collected	21959	30204	15844
Independent reflections	5874 [R_{int} = 0.0193]	6475 [R_{int} = 0.0458]	3158 [R_{int} = 0.0275]
Data/restraints/parameters	5874/1/415	6475/0/451	3158/0/226
Goodness-of-fit on F²	1.141	1.186	1.133
Final R indexes [I>=2σ (I)]	R_1 = 0.0517 wR$_2$ = 0.1367	R_1 = 0.0823 wR$_2$ = 0.2040	R_1 = 0.0744 wR$_2$ = 0.1940
Final R indexes [all data]	R_1 = 0.0537 wR$_2$ = 0.1380	R_1 = 0.0900 wR$_2$ = 0.2095	R_1 = 0.0767 wR$_2$ = 0.1971
Largest diff. peak/hole / e Å^{-3}	0.46/-0.37	0.42/-0.40	1.53/-0.37

Section S4. Single-crystal transistors

## Modification of SiO$_2$ wafer with OTS

The substrate was a heavily doped n-type Si wafer with a 300 nm thick SiO$_2$ layer. The substrates were cleaned with deionized water, piranha solution (H$_2$SO$_4$:H$_2$O$_2$ = 7:3), deionized water, and isopropanol successively. The clean wafers were dried under vacuum at 90°C for 1.5 hrs to eliminate moisture. After cooling to room temperature, one drop of OTS was placed on the wafer side. This system was then heated up to 120°C for 2 hrs under vacuum. After cooling down to room temperature, the wafers were washed under ultrasonic by n-hexane, chloroform, and isopropanol successively, and then blow-dried by N2 and ready for use.

## XRD, AFM, and TEM study of single-crystal samples

XRD measurements are carried out on PANalytical Empyrean (Japan). AFM images of single crystals were obtained by using a Cypher ES of Asylum Research atomic force microscope in the air. TEM and SAED measurements are carried out on a JEM 1011 (Japan).
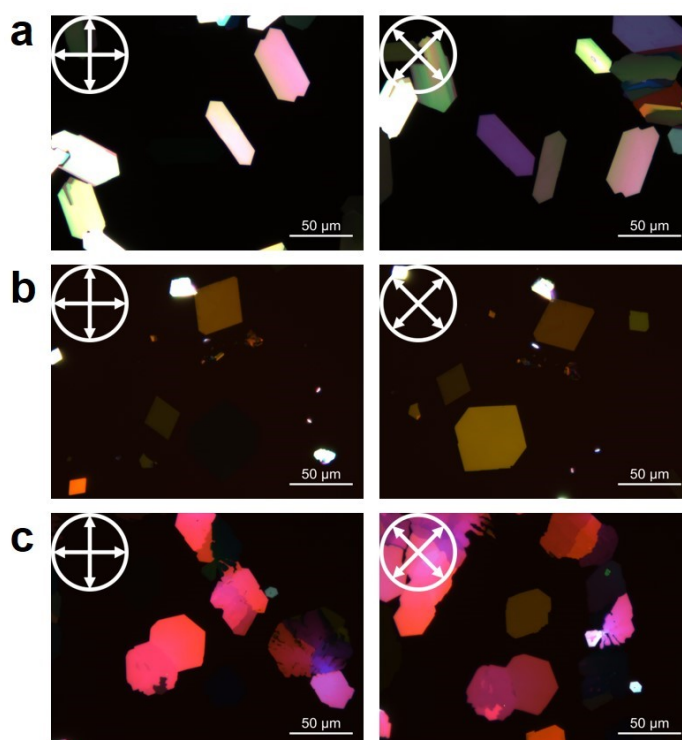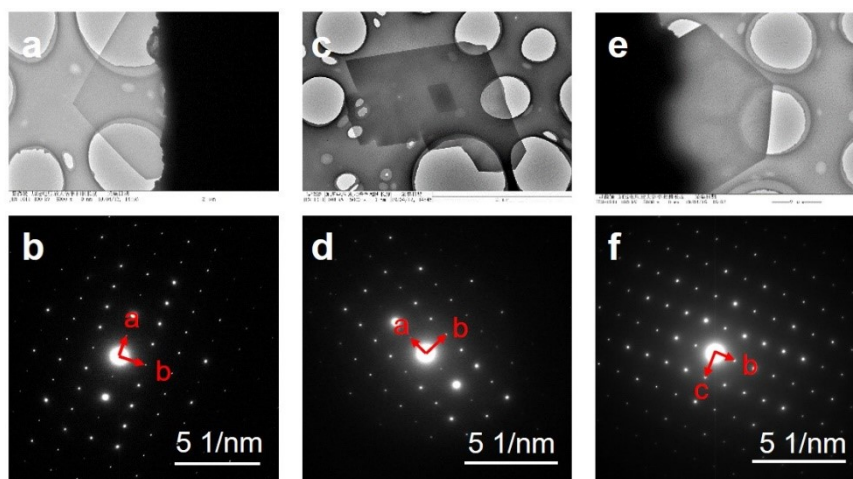

Figure S2 The polarized optical microscope images of (a) **5-BTA**, (b) **5-BTVA**, and (c) **5-BTEA**.
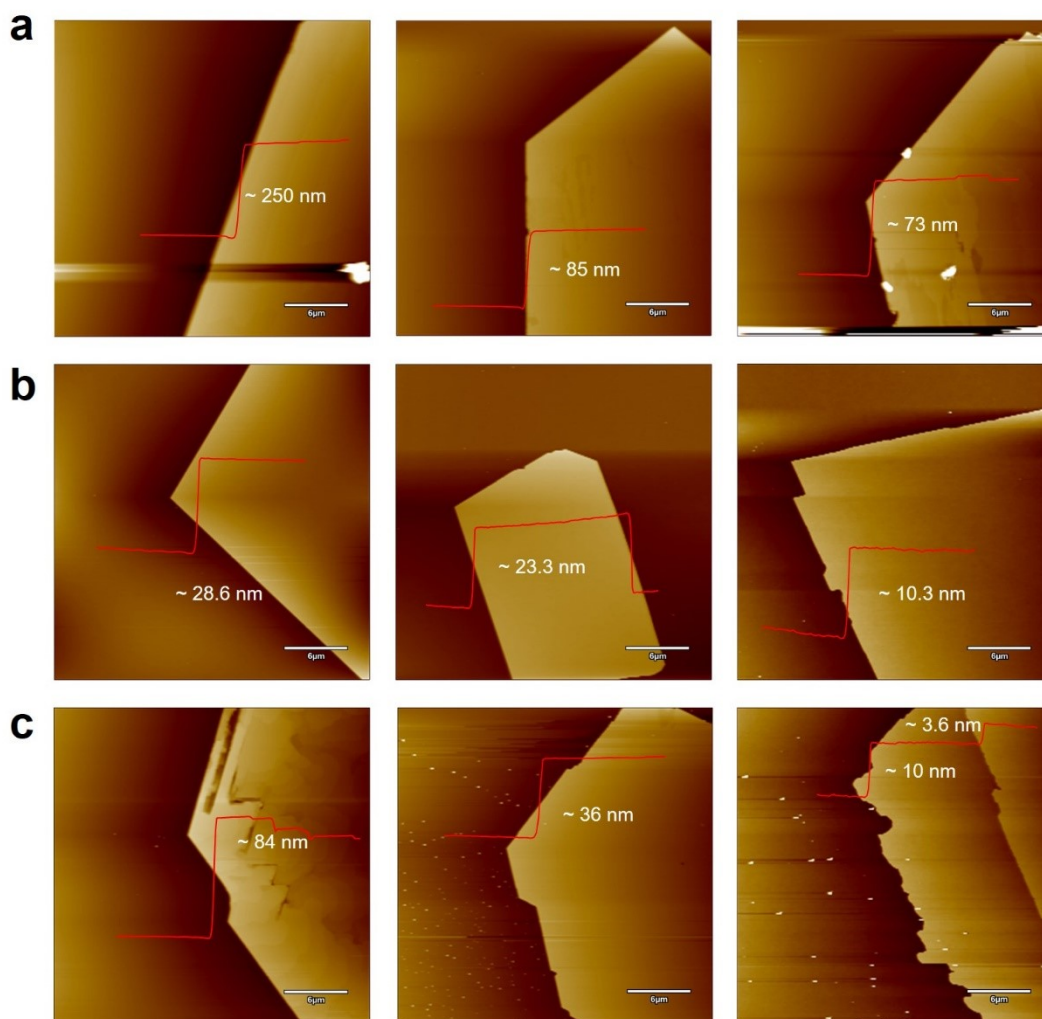
Figure S3 The single-crystal AFM images of three molecules with different thickness. (a), **5-BTA**, (b), **5-BTVA,** and (c), **5-BTEA**. Scale bar, 6 μm.
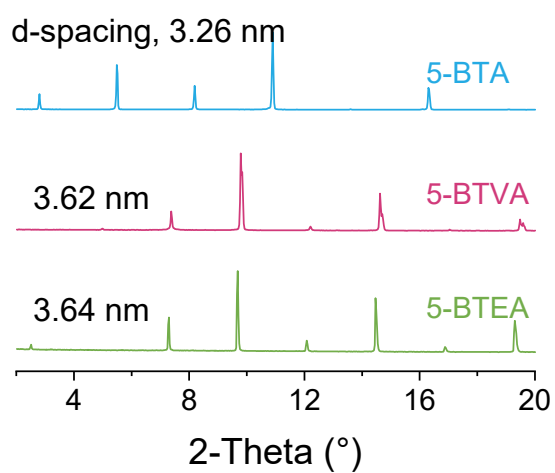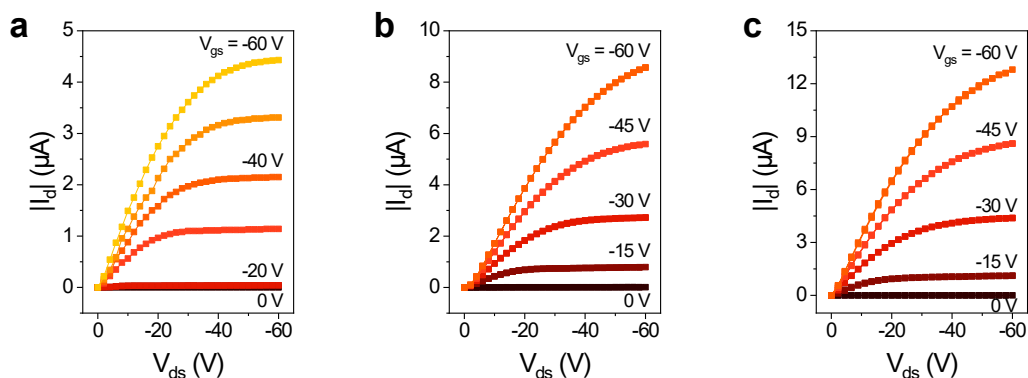

Figure S4 Out-of-plane 2D XRD patterns of three crystalline samples.

Figure S5 The TEM images and corresponding SAED patterns of three single crystals. (a-b), **5-BTA**, (c-d), **5-BTVA,** and (e-f), **5-BTEA**.
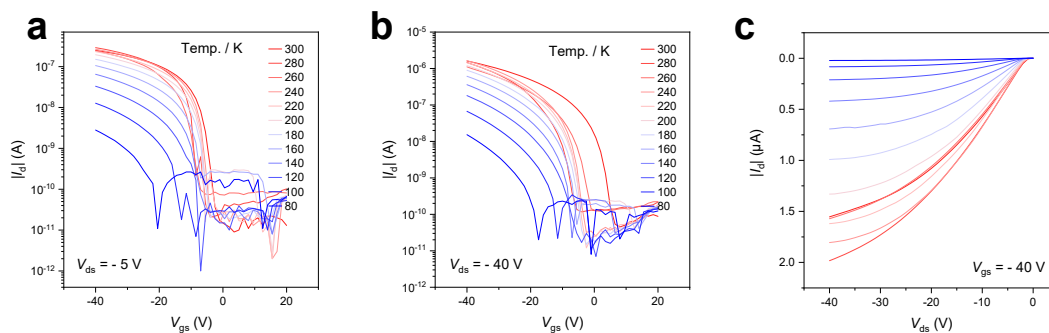
Fabrication of single-crystal transistors

Single crystal devices were fabricated using the transfer "Au stripes" technique.

Figure S6 Typical transfer and output curves of three single-crystal transistors. (a-b), **5-BTA**, (c-d), **5-BTVA,** and (e-f), **5-BTEA**.

## Temperature dependence of charge transport

The field-effect transistors temperature-dependent measurements are carried out on Lake Shore cryotronics (U.S.A) under ~ 5×10^{-7} mbar vacuum.


Figure S7 The transfer curves at (a) linear and (b) saturation regimes and (c) output curves with temperature from 300 cooling to 80 K of **5-BTA** single-crystal transistor.
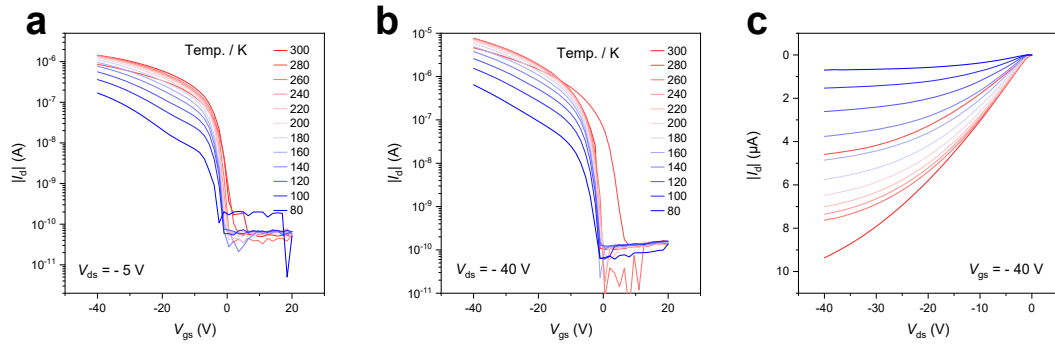
Figure S8 The transfer curves at (a) linear and (b) saturation regimes and (c) output curves with temperature from 300 cooling to 80 K of **5-BTVA** single-crystal transistor.
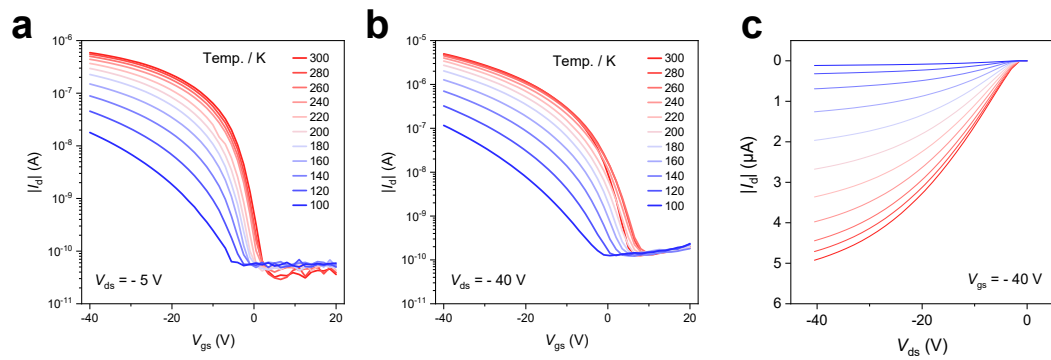
Figure S9 The transfer curves at (a) linear and (b) saturation regimes and (c) output curves with temperature from 300 cooling to 100 K of **5-BTEA** single-crystal transistor.
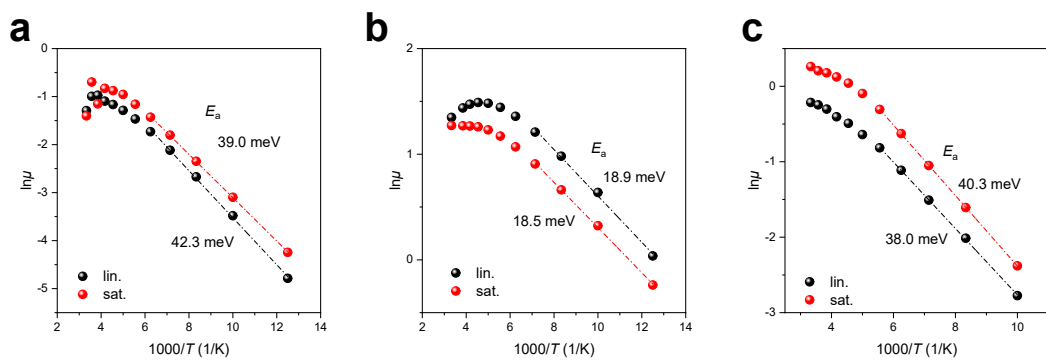
Figure S10 The plot of 1000/T – lnμ and activation energy E_a extracted from the slope according to $\mu = \mu_0 \exp(-E_a / k_B T)$.