Supporting Information

Tuning Crystal Polymorphs of a π-Extended Tetrathiafulvalene-based Cruciform Molecule towards High-Performance Organic Field-Effect Transistors

Linlin Feng,[a,b] Huanli Dong,[b,*] Qingyuan Li,[a,b] Weigang Zhu,[b] Gege Qiu,[a,b] Shang Ding,[a,b] Yang Li,[b] Mikkel A. Christensen,[c] Christian R. Parker,[c] Zhongming Wei,[d] Mogens Brøndsted Nielsen,[c] Wenping Hu[b,e]

[a]Beijing Key Laboratory for Optical Materials and Photonic Devices, Department of Chemistry, Capital Normal University, Beijing 100048, China.

[b]Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

[c]Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100, Copenhagen Ø, Denmark.

[d]State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China.

[e]Tianjin Key Laboratory of Molecular Optoelectronic Sciences, Department of Chemistry, School of Sciences, Tianjin University, & Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China.

Section 1. Detailed Experimental Conditions

Cleaning of substrates. First the Si/SiO_2 substrates were cleaned with piranha solution (H_2O_2/H_2SO_4 = 1:2) for 10 min and then washed with deionized water and then isopropyl alcohol to remove the residual solvent or water. Subsequently the substrates were dried with high-purity nitrogen gas and cleaned with oxygen plasma (about 5 min). Finally the clean wafers were put in vacuum oven at 90 °C for 1 h and then modified with OTS at 120 °C for 2 h. The modified substrates were cleaned with hexane, chloroform and isopropyl alcohol successively for use in following.

Single crystal preparation. For both IF-TTF solutions, 25 μL solutions were dropped on 1×1 cm^2 OTS-modified Si/SiO_2 substrates which were put in weighing bottles. Single crystals were obtained after the solvent evaporation at the room temperature overnight. Then the crystals were annealed in vacuum at 80°C for α-phase single crystal and 120°C for β-phase before the fabrication of the devices.

Device fabrication. Top-contact bottom-gate devices single crystal transistors were fabricated through an Au-layer stamping technique[1]. Organic field-effect transistor characteristics were carried out at room temperature in air on a Keithley 4200 SCS and Micromanipulator 6150 probe station and the mobility was extracted from the saturation region by using the equation of $I_{DS}=(W/2L)C_i\mu(V_G-V_T)^2$.

Characterizations. The microscope images of the single crystals were acquired by an Olympus BX51 optical microscope (Vision Engineering Co., UK). The structures were analyzed by XRD (Rigaku D/max 2500) and SAED patterns (TECNAI T20 electron microscope (FEI, USA)). Single crystal data were obtained using a Single crystal X- ray diffraction (Rigaku ST Saturn 724+).

Section 2. Supporting data

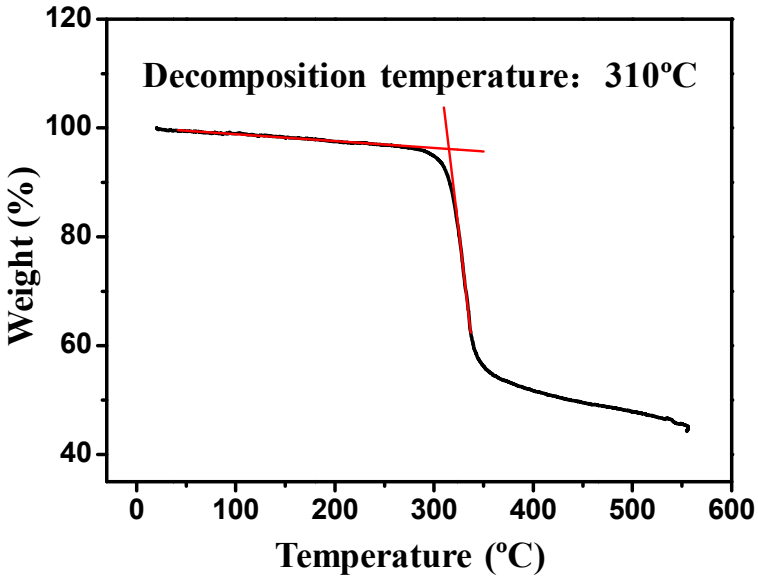

Figure S1. TGA of IF-TTF.

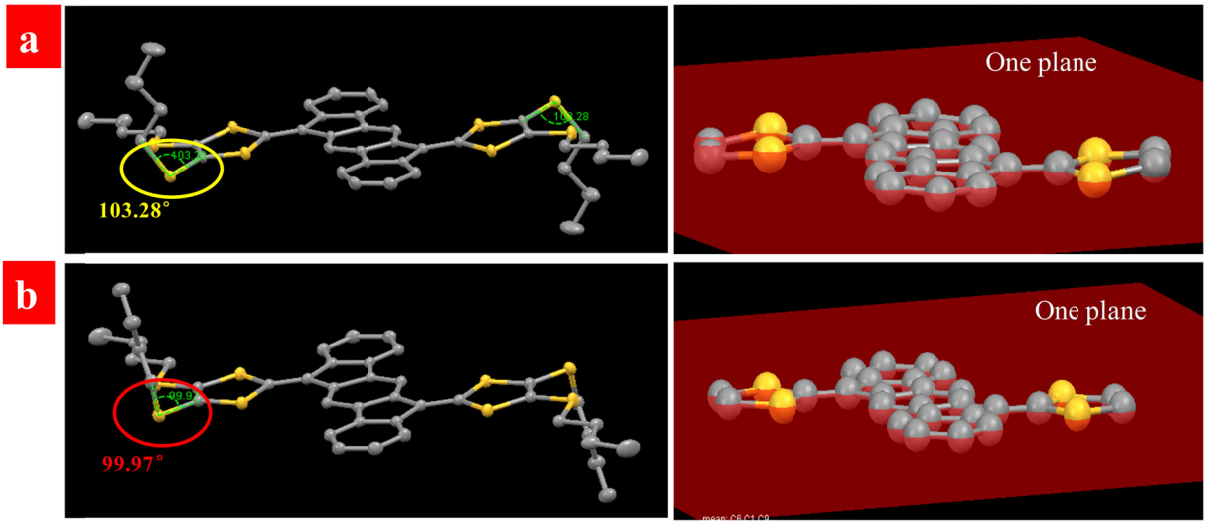

Figure S2. The different intersection angles between the molecular conjugated plane of IF and TTF units (right) and the SBu substituent groups that out of the planes for α-phase (a) and β-phase (b) crystals.

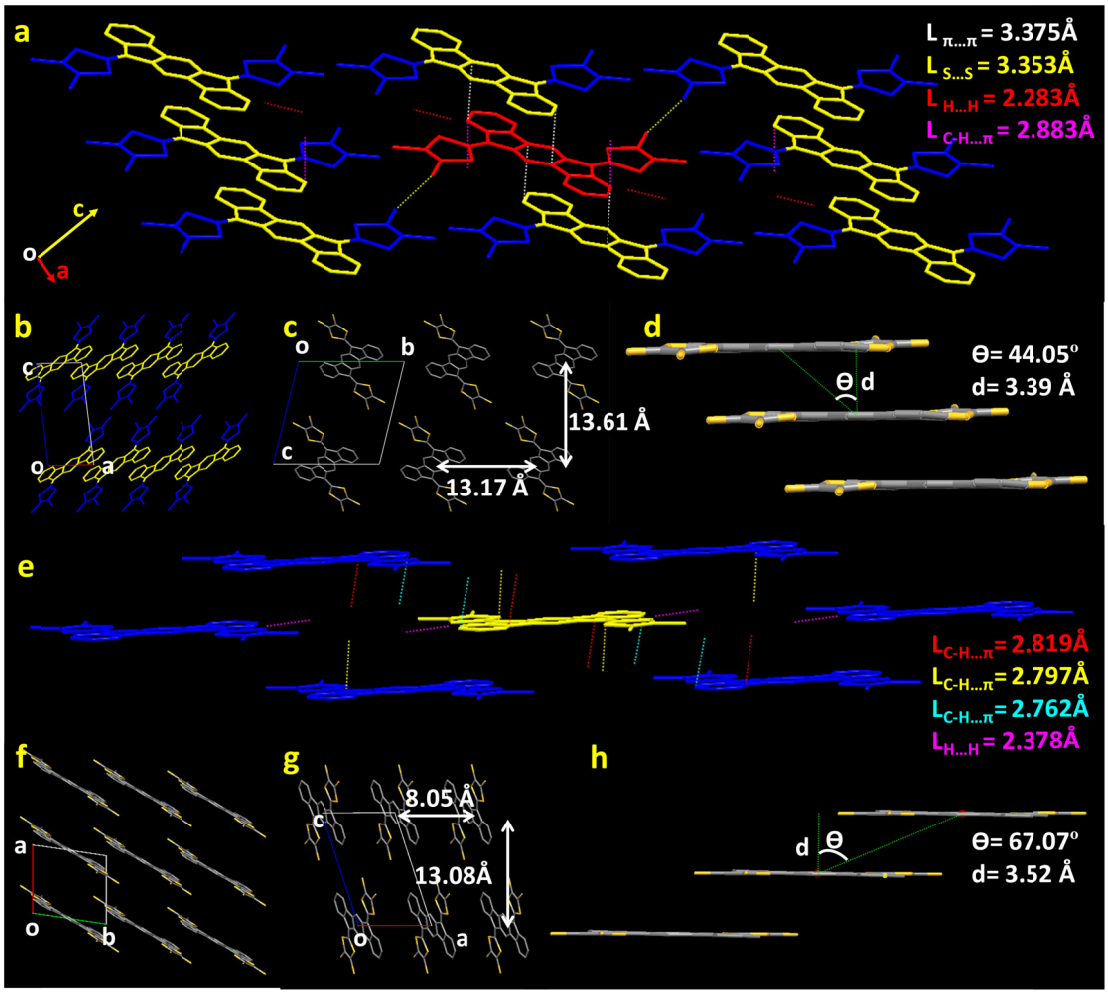

Figure S3. (a) View interactions of α-phase crystal polymorph: one molecular with eight neighbors. View of the molecular packing structure along the *b*-axis (b) and the layered structure along the cell *a*-axis (c). (d) Stacking diagram showing π…π interaction in α-phase crystal polymorph. (e) View interactions of β-phase crystal polymorph: one molecular with six neighbors. View of the molecular packing structure along the *c*-axis (f) and the layered structure along the cell *b*-axis (g). (h) Stacking diagram showing π…π interaction in platelet-shaped crystal polymorph (all the alkyl chains have been omitted for clarity).

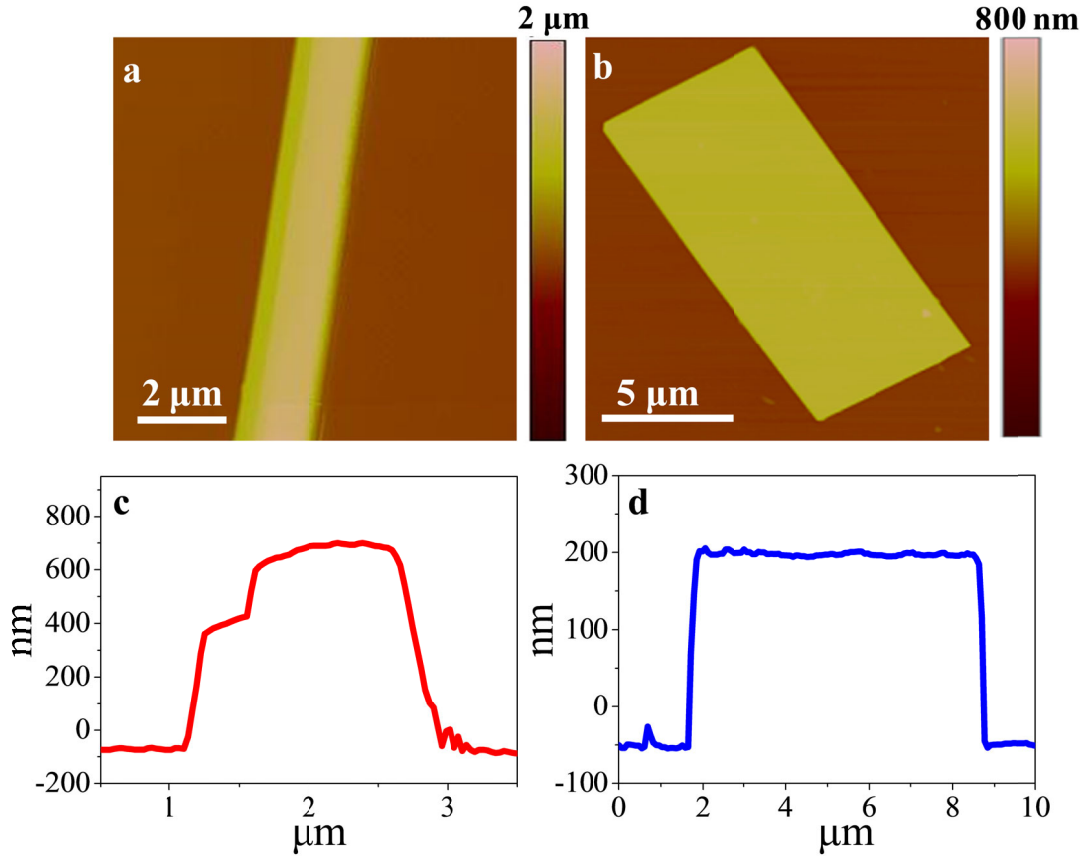

Figure S4. AFM images and height curves of α-phase (a,c) and β-phase (b,d) IF-TTF single crystals.

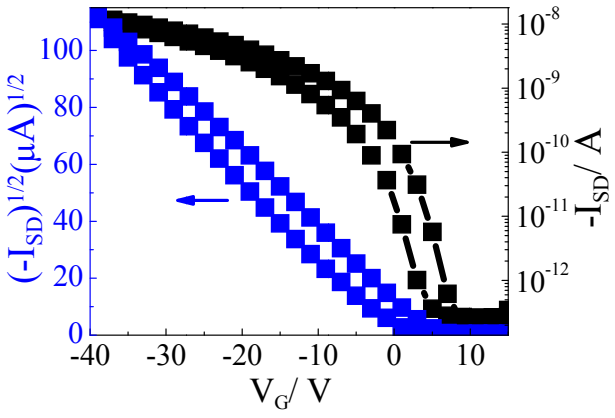

Figure S5. The hysteresis transfer curves of IF-TTF crystal-based transistors.

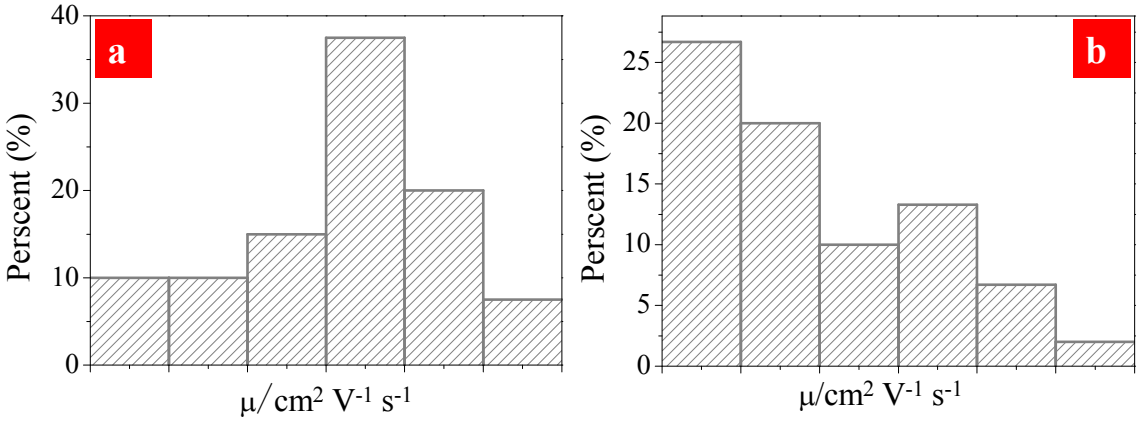

Figure S6. The bar charts of the frequency distributions of the 40 devices for α-phase a) and β-phase b) IF-TTF crystals

Table S1 The comparison of detailed structure parameters for α-phase and β-phase IF-TTF crystals

Identification code	**mx4406 (α-phase)**	**CCDC:962757 (β-phase)**
Crystal size (mm^3)	0.38 × 0.06 × 0.03	0.36× 0.26× 0.06
Unit cell dimensions	*a* = 5.357(4) Å *b* = 13.520(10) Å *c* = 14.010(10) Å *α*= 102.979(18) Å *β*= 94.587(18) Å *γ*= 90.165(13) Å	*a* = 8.4030(6) Å *b* = 9.0350(11) Å *c* = 14.0030(13) Å *α*= 103.453(19) Å *β*= 106.211(12) Å *γ*= 94.229(10) Å
Space group	P-1	P-1
Crystal system	Triclinic	Triclinic
Volume ($Å^3$)	985.4	981.833
R-factor	7.34	3

Section 3. Crystal data and structure refinement for α-phase IF-TTF crystal

Identification code	mx4406	
Empirical formula	C_{42} H_{46} S_8	
Formula weight	807.27	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	*a* = 5.357(4) Å	*α*= 102.979(18)Å
	b = 13.520(10)Å	*β*= 94.587(18)Å
	c = 14.010(10)Å	*γ*= 90.165(13)Å
Volume	985.4(12) Å^3	
Z	1	
Density (calculated)	1.360 Mg/m^3	
Absorption coefficient	0.484 mm^{-1}	
F(000)	426	
Crystal size	0.38 × 0.06 × 0.03 mm^3	
Theta range for data collection	1.497 to 27.541Å	
Index ranges	-6<=h<=6, -17<=k<=17, -18<=l<=17	
Reflections collected	11642	
Independent reflections	4474 [R(int) = 0.1306]	
Completeness to theta = 26.000°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.1699	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4474 / 0 / 228	
Goodness-of-fit on F^2	1.110	
Final R indices [I>2sigma(I)]	R1 = 0.0734, wR2 = 0.1619	
R indices (all data)	R1 = 0.0923, wR2 = 0.1733	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.443 and -0.445 e.Å^{-3}	

Reference

[1] Q. Tang, L. Jiang, Y. Tong, H. Li, Y. Liu, Z. Wang, W. Hu, Y. Liu, D. Zhu, *Adv. Mater.*, 2008, **20**, 2947.