



Tuning crystal polymorphs of a π -extended tetrathiafulvalene-based cruciform molecule towards high-performance organic field-effect transistors

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ABSTRACT It is a common phenomenon for organic semiconductors to crystallize in two or more polymorphs, leading to various molecular packings and different charge transport properties. Therefore, it is a crucial issue of tuning molecular crystal polymorphs (i.e., adjusting the same molecule with different packing arrangements in solid state) towards efficient charge transport and high performance devices. Here, the choice of solvent had a marked effect on controlling the growth of α -phase ribbon and β -phase platelet during crystallization for an indenofluorene (IF) π -extended tetrathiafulvalene (TTF)-based cruciform molecule, named as IF-TTF. The charge carrier mobility of the α -phase IF-TTF crystals was more than one order of magnitude higher than that of β -phase crystals, suggesting the importance of reasonably tuning molecular packing in solid state for the improvement of charge transport in organic semiconductors.

Keywords: organic semiconductor, crystal polymorphs, tetrathiafulvalene-based cruciform molecule, field-effect transistor, charge carrier mobility

Functional organic molecules that may serve as the active components for organic electronics, such as organic field-effect transistors (OFETs), switches, or rectifiers has attracted wide interest in recent years [1–4]. Among them, tetrathiafulvalene (TTF), first discovered by Wudl *et al.* [5] in 1970, has been seen as a promising building block for developing molecular electrical wires [6] and

high performance organic semiconductors because of its unique redox-active properties, being reversibly oxidized in two one-electron steps [7–10] and having a nearly planar molecular structure and strong intermolecular π - π and S...S interactions facilitating charge transport. To date, a series of TTF-based organic semiconductors with linear-extended conjugation have been synthesized, and excellent charge carrier transport properties in OFETs [1,2,11–15] and molecular devices [16] were demonstrated. Different from the one-dimensional TTF-based molecules widely investigated in the past, we focused on combining dithiafulvalene (DTF; “TTF half unit”) and other functional molecular units to design cruciform-like molecular structures (that is, two orthogonally oriented π -systems). One aim was to achieve good and tunable conducting properties by virtue of the different conjugation pathways that exist between the individual parts of the molecule [17–23]. These DTF-based cruciform molecular wires have demonstrated potential promising applications in molecular electronics and also provided a good platform for the investigation of the dependence of conducting properties on their molecular structures [24–26]. As a continuation of our work on such extended TTF compounds, it is interesting to further investigate their applications in organic electronic devices, such as OFETs, the basic component of organic circuits. Here, we present a comprehensive study

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on an indenfluorene-extended TTF recently reported [23] (IF-TTF; Fig. 1a), tuning its crystal polymorphs, analyzing their molecular structures and measuring their electrical transport properties. The results demonstrated that the obtained charge carrier mobility of the α -phase IF-TTF ribbon crystals based-single crystal organic transistors was more than one order of magnitude higher than that of β -phase platelet crystals, with the highest charge carrier mobility over $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, indicating the potential applications of the DTF-based π -extended cruciform molecules in OFETs and the importance of tuning molecular crystal polymorphs for improvement of their electrical performance.

To probe the effect of DTF units on the electron distribution, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of IF-TTF are shown in Fig. 1b. It can be seen that on HOMO and LUMO orbitals, the electron distribution on the whole molecule demonstrates a quasi-two-dimensional (2D) distribution, suggesting the extended π -conjugation on the whole molecular structure. It also should be stated that a stronger electron-weight is distributed along the direction of DTF-substituted vertical conjugation backbones, indicating the ability of losing electrons of IF-TTF molecules to the electrodes for the formation of efficient hole charge transport channels in organic electronic devices. The calculated HOMO and LUMO energy levels are -4.79 eV and -1.62 eV , respectively, with the corresponding experimental values of -4.64 eV for HOMO and -2.09 eV for LUMO obtained through the cyclic voltammetry curves [23]. Additionally, a good thermal stability with the decomposition at around 310°C for IF-TTF was observed by thermo-gravimetric analysis (TGA) (see Fig. S1, Supplementary Information).

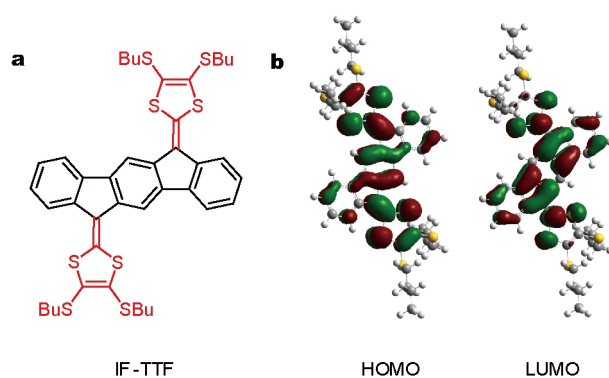


Figure 1 (a) Molecular structure of IF-TTF. (b) The calculated HOMO and LUMO orbitals of IF-TTF based on B3LYP/6-31G(d,p) [27].

The extended 2D π -conjugation of IF-TTF (proposed from the 2D electron distribution and the good coplanar conjugated structure obtained from its single crystal data as following), the appropriate energy levels, and the good thermal stability of IF-TTF indicate its promising applications in electronic devices. To investigate the intrinsic charge transport of IF-TTF compound, micro/nano- single crystals of IF-TTF were prepared, as we know that organic single crystals are regarded as the best candidates for correctly evaluating the charge transport property of semiconducting materials due to their perfect molecular packing and no grain boundaries, low-density defects [28–30]. Very interestingly, two different crystals phases of IF-TTF could be easily prepared in a good controllability through the simple self-assembly by drop casting IF-TTF solutions, which is independent of the substrates, such as bare SiO_2 and octadecyltrichlorosilane (OTS)-modified SiO_2 substrates. It was found that when with chloroform as the solvent, the ribbon-shaped α -phase IF-TTF single crystals were generally obtained in large area with the ultra-long length of several hundreds of micrometers or even beyond one millimeter and width below several micrometers, corresponding to a high length/width ratio of largely over 100 (Fig. 2a). However, using toluene as the solvent promoted the platelet/block-shaped β -phase, and IF-TTF single crystals were formed generally with length of tens micrometers and width of several micrometers (Fig. 2b), indicating the strong solvent effect on molecular aggregation [23] and further assembly for IF-TTF, which is very popular for TTF-derived molecules [31–33] and other organic systems [34–36]. Fortunately, by carefully controlling the slow solvent evaporation from their corresponding saturated chloroform or toluene solution for crystal growth, enough large ribbon (named as α -phase) and block (named as β -phase) single crystals of IF-TTF were successfully obtained separately for single crystal data analysis. The X-ray crystallographic results demonstrate that the α -phase crystal (obtained based on crystal with size of $0.38 \text{ mm} \times 0.06 \text{ mm} \times 0.03 \text{ mm}$) belongs to triclinic $P-1(2)$ space group with lattice constants of $a = 5.36 \text{ \AA}$, $b = 13.52 \text{ \AA}$, $c = 14.01 \text{ \AA}$ and $\alpha = 102.98^\circ$, $\beta = 94.59^\circ$, $\gamma = 90.17^\circ$ (CCDC: 1505740). The β -phase IF-TTF single crystal belongs to triclinic $P-1(2)$ space group, with lattice constants of $a = 8.40 \text{ \AA}$, $b = 9.04 \text{ \AA}$, $c = 14.00 \text{ \AA}$ and $\alpha = 103.45^\circ$, $\beta = 106.21^\circ$, $\gamma = 94.23^\circ$ (CCDC: 962757) [23]. Good coplanar conjugation between the DTF and IF units in one IF-TTF molecule is demonstrated by the detailed structure analysis, with different angles of 103.28° and 99.97° between the molecular conjugated plane and the

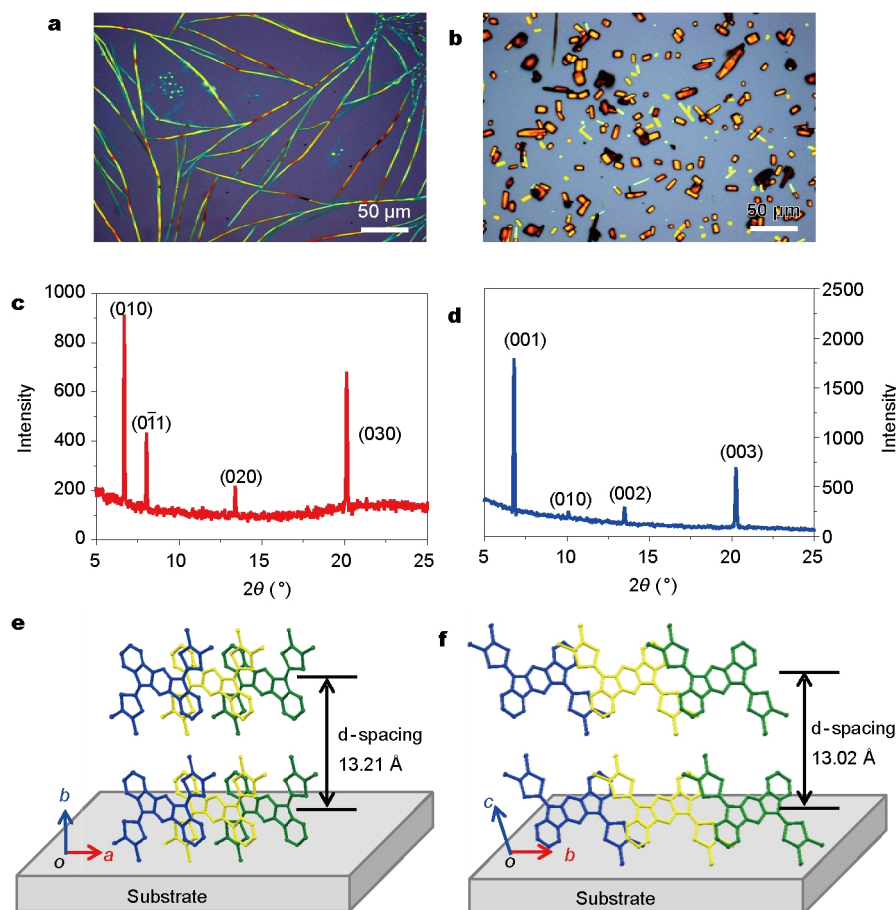


Figure 2 (a, b) Optical microscopy images and (c, d) XRD patterns of the α -phase ribbon and β -phase block IF-TTF crystals. (e, f) The proposed preferable molecular packing modes on the substrate achieved from the XRD results.

S-Bu substituent groups that are out of the planes for α -phase and β -phase crystals, respectively (Fig. S2). Just such a slightly unit cell structure results in obviously different molecular interactions/packing in their crystals and crystal growth behaviors. In α -phase crystals, one IF-TTF molecule is connected with six neighboring molecules through strong $\pi\cdots\pi$, S \cdots S, H \cdots H, C-H $\cdots\pi$ interactions, demonstrating a layer-by-layer molecular packing with discrete columns (Figs S3a–d). The spacing distance of two adjacent columns is 13.52 Å and the interlayer π - π stacking distance is around 3.375 Å. The slipping angle created by the disposition of centroid of the fused ring planes is 44.05° (Fig. S3d). In comparison, in β -phase single crystals, one IF-TTF molecule is connected with six neighboring molecules through two types of C-H $\cdots\pi$ and H \cdots H interactions (Figs S3e–h). Compared to α -phase crystals, there are no S \cdots S interactions observed in β -phase crystal phase and relatively larger $\pi\cdots\pi$ stacking distance of 3.52 Å coming from the overlap of one end benzene ring and DTF unit between the neighboring molecules. The

spacing distance of two adjacent columns and two adjacent layers are 8.05 Å and 13.08 Å, respectively. The slipping angle created by the disposition of centroid of the fused ring planes is 67.07° (Fig. S3h).

The characteristic X-ray diffraction (XRD) patterns of two phases for IF-TTF crystals are shown in Figs 2c and d, showing a series of sharp reflection with the strongest peak at $2\theta = 6.68^\circ$ (corresponding to $d = 13.21$ Å) and $2\theta = 6.78^\circ$ (corresponding to $d = 13.02$ Å), respectively. All the peaks in the XRD patterns could be well indexed according to their single crystal data of α -phase and β -phase, respectively, indicating the pure IF-TTF crystal phases obtained by simple selection of the solvents. The results demonstrate that the (0 k 0) planes in α -phase crystals and the (00 l) planes in β -phase crystals are preferably parallel to the substrate. The schematic molecular packing structure related to the substrate are shown in Figs 2e and f, where the IF-TTF molecules are preferably standing on the substrate with different title angle of 77.9° in α -phase and 73.73° in β -phase, respectively, forming the typical

layer-by-layer packing structure. To probe the molecular growth model, typical transmission electron microscopy (TEM) was further performed. The TEM images of an individual ribbon and platelet crystal of IF-TTF and their corresponding selected-area electron diffraction (SAED) pattern are shown in Figs 3a and b, respectively. During the experiment, no change of the SAED patterns was observed along the whole ribbon and platelet crystals, indicating the single crystal characteristic for both ribbon and platelet crystals. According to the single crystal data of α -phase crystals, its SAED pattern could be well indexed with diffraction spots from the ac planes, agreeing with that $(0k0)$ planes parallel to the substrate obtained from its XRD patterns. Detailed analysis indicate that the single crystal ribbons grow along the $[100]$ direction. Additionally, the index of SAED patterns for β -phase crystals indicates its crystal growth direction along the $[010]$ axis. The $[100]$ direction in α -phase and $[010]$ in β -phase crystals are both corresponding to their π - π stacking directions, indicating efficient charge transport along the direction (Figs 3c and d). Additionally, the different π - π stacking distance and overlaps of α -phase and β -phase crystals along the charge transport direction (Figs 3c-f) suggest their different transporting properties, which provides us a good platform for the investigation of stacking structure and property relationship. Moreover, both the crystal surface

of α -phase and β -phase of IF-TTF crystals are very smooth as estimated by atomic force microscopy (AFM), which is beneficial for good contact and electron injection in devices (Fig. S4).

To investigate the charge transport of IF-TTF and elucidate the relationship between molecular packing structures and properties in α -phase and β -phase single crystals, top-contact bottom-gate IF-TTF single crystal transistors were fabricated based on the OTS-modified Si/SiO₂ substrates (SiO₂ dielectric thickness: 300 nm with $C = 11$ nF cm⁻²). Before the device fabrication, the IF-TTF crystals were first heat treated at 80°C for α -phase and 120°C for β -phase for 2 h to remove any residual solvent on the crystals and substrate which could act as the electron traps being unfavorable for charge transport. In order to reduce the damage of heat radiation during vacuum electrodes deposition, we adopted a “gluing gold film” technique developed previously in our group [28] to *in-situ* construct the top source and drain electrodes on IF-TTF crystals. Additionally, for achieving a good contact between crystals and electrodes in the devices, we preferentially selected the relatively thin IF-TTF crystals, that were generally in blue color simply estimated from the optical microscopy due to different refractive index of the different thick crystals related to the substrate [37]. The optical microscopy images of the typical constructed IF-TTF ribbon and platelet crystal transistors are shown in Figs 4a and b, respectively. Around 40 devices of α -IF-TTF and β -IF-TTF crystals were fabricated and the corresponding bar charts of the frequency distributions are shown in Fig. S6. Representative output and transfer characteristics of these devices are demonstrated in Figs 4c-f. It can be seen that both α - and β -phase IF-TTF single crystal transistors demonstrate typical p-type field-effect transporting property with good gate voltage modulation. Relatively weak contact resistance and hysteresis were observed from the output and transfer curves (Fig. S5), suggesting the good organic-electrode contact and high-quality interface between IF-TTF crystals and the OTS-modified SiO₂ substrate. From the saturation regime of the transfer characteristics, the mobility is calculated according to the linear fitting of $(-I_{SD})^{1/2}$ versus V_G curve. The obtained average and highest mobilities for α -phase IF-TTF crystal transistors are 0.32 and 1.44 cm² V⁻¹ s⁻¹, respectively. While for the β -phase IF-TTF crystal transistors, the average and highest mobilities are only 3.95×10^{-2} and 0.28 cm² V⁻¹ s⁻¹, around one order magnitude lower than that of α -phase IF-TTF crystal transistors. All the IF-TTF-based transistors exhibit high source-drain on/off current ratio of over 10³ and low threshold voltage

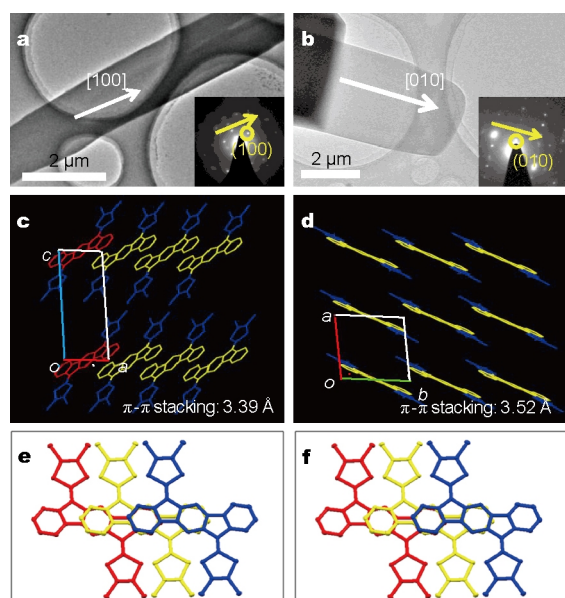


Figure 3 (a, b) TEM images of α -phase and β -phase IF-TTF crystals and their corresponding SAED patterns. (c, d) The deduced molecular packings in α and β -phase crystals. (e, f) The π - π stacking overlap in α -phase and β -phase crystals seen along their growth direction axis.

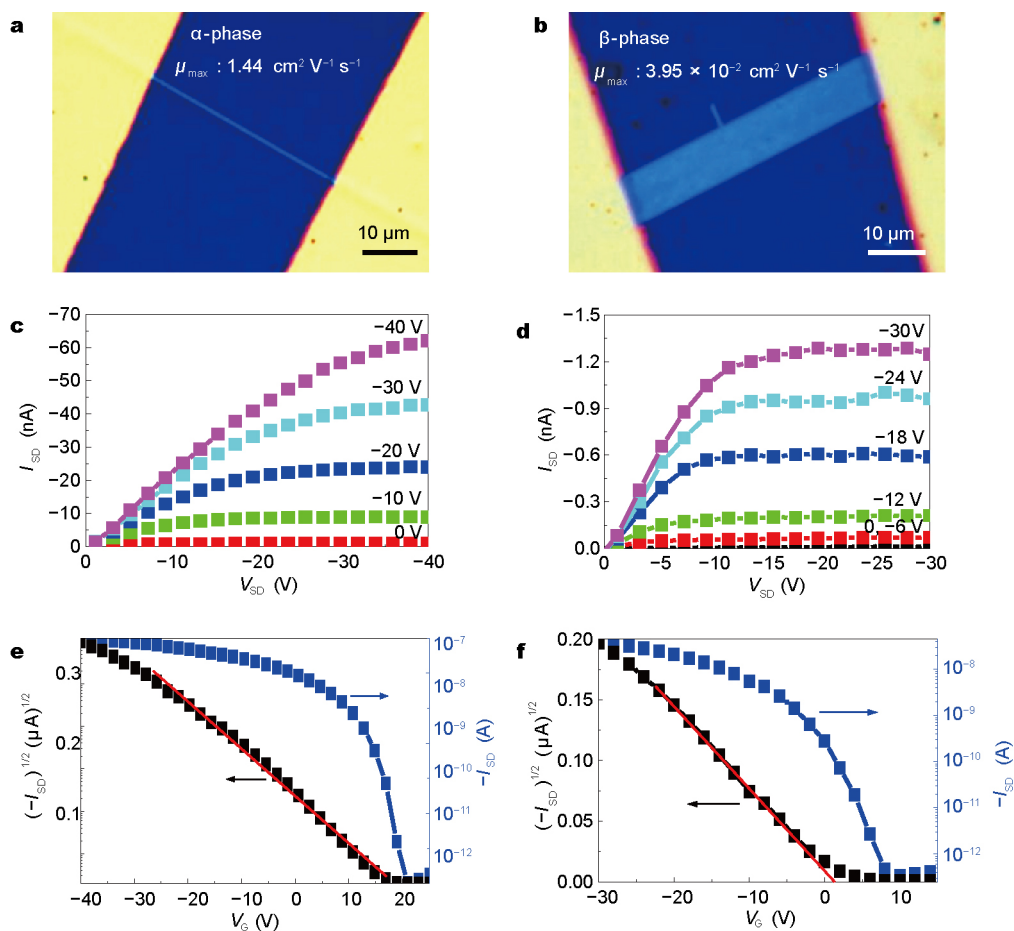


Figure 4 Optical images of device structures based on α -phase (a) and β -phase (b) single crystals. Typical output and transfer characteristics of IF-TTF based transistors based on (c, e) α -phase single crystal ($V_{SD} = -40$ V) and (d, f) β -phase single crystal ($V_{SD} = -30$ V).

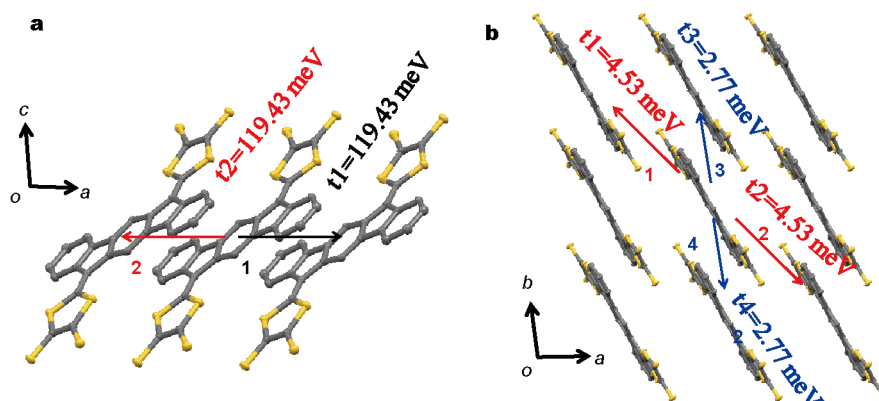


Figure 5 Illustrations of molecular packing structures and transfer integrals for the nearest neighboring molecular pairs considered in the calculations (a) for α -phase crystal and (b) for β -phase crystal based on the direct integration method ($V = \langle \Phi_{HOMO} | F_0 | \Phi_{HOMO} \rangle$) with site-energy correction [38].

below -5 V. The higher charge carrier transport obtained based on α -phase IF-TTF crystal transistor is attributed to the more condensed molecular packing in this state, which

is consistent with its relatively larger transfer integral (119.43 meV) than that of β -phase crystals (4.53 and 2.77 meV) by the theoretical calculations (Fig. 5). More detail-

Table 1 The comparison of the charge transport property for α -phase and β -phase IF-TTF crystals

Identification code	CCDC: 1505740 (α -phase)	CCDC: 962757 (β -phase)
Reorganization energy	326.20 meV	
Transfer integral (meV)	Path 1: 119.43(<i>a</i>) Path 2: 119.43(- <i>a</i>)	Path 1: 4.53(<i>a</i> - <i>b</i>), Path 3: 2.77(<i>b</i>) Path 2: 4.53(- <i>a</i> + <i>b</i>), Path 4: 2.77(- <i>b</i>)
Calculated mobility μ (cm ² V ⁻¹ s ⁻¹)	0.98 (along <i>a</i> axis)	0.0037 (along <i>b</i> axis)
Measured mobility μ_{\max} (cm ² V ⁻¹ s ⁻¹)	1.44 (along <i>a</i> axis)	0.28 (along <i>b</i> axis)

led comparison information for α -phase and β -phase crystals of IF-TTF are summarized in Table 1. Here for the first time the achieved high charge carrier mobility, on/off ratio and the low threshold voltage of DTF-derivative-based transistors suggest the promising potential applications of DTF-extended organic semiconductors in OFETs with the consideration of rationally controlling their crystal polymorphs.

In summary, two crystal polymorphs of IF-TTF were controllably achieved through the simple solvent selection, the structures of which were comprehensively characterized. The crystal polymorph-dependent carrier mobility was investigated based on their single crystals field-effect transistors. Compared with β -phase IF-TTF single crystals, the α -phase IF-TTF single crystals demonstrate more than one order of magnitude higher charge carrier mobility with the highest carrier mobility value around 1.44 cm² V⁻¹ s⁻¹ and the on/off ratio of 10³, suggesting the potential application of such type semiconductors in OFETs. This study also provides the guideline for tuning molecular crystal polymorph and molecular structure design for achieving high electrical property.

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Author contributions Dong H and Hu W conceived and designed the experiments. Christensen MA, Parker CR and Nielsen MB synthesized the compound. Feng L performed the experiments. Zhu W contributed to the structure analysis. Li Y contributed to the theoretical calculations. Dong H, Feng L, Hu W and Nielsen MB co-wrote and revised the manuscript. All the authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information The experiment data are available in the online version of the paper.



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通过晶相调控实现高性能十字形TTF分子场效应晶体管器件构筑

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摘要 有机分子溶剂的选择对于调控不同晶相来说有着关键性作用. 本文通过两种溶剂的调控, 成功得到茚并芴四硫富瓦烯(IF-TTF)两种不同的晶相— α 相带状晶体和 β 相片状晶体, 并对两种晶相的内部分子排列堆积情况进行了一系列的对比分析. 结果表明场效应电荷传输能力随着晶相的不同而有所差异, 直接证明了分子堆积的合理调控对实现有机半导体材料高性能电荷传输性能的重要性.