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Introduction

Since the discovery of the first organic metal tetrathiafulvalene-7,7,8,8-tetracyanoquinodimethane (TTF-TCNQ) about forty years ago,¹ tetrathiafulvalene (TTF) and its derivatives have been successfully used as building blocks for charge transfer salts, giving rise to a multitude of organic conductors and superconductors, as well as for the preparation of a wide range of molecular materials.^{2,3} TTF derivatives are mostly achieved by simple synthetic paths and are easily chemically modified; they are generally soluble in common solvents and benefit the solution-processable devices; they show planar molecular conformation and strong intermolecular interactions in the solid state induced by $\pi \cdots \pi$ stacking and S \cdots S interactions; and they show good electron donor ability with the highest occupied molecular orbital (HOMO) levels close to the work function of usual metallic electrodes, affording a low energy barrier for charge injection from metal electrodes into their active layers.4,5 Considering thus all the above, TTF derivatives also show promise to be good candidate molecules

Synthesis and properties of T-shaped organic conjugates based on 3,6-diarylpyridazine-fused tetrathiafulvalenet

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A facile synthetic approach to the π -expanded tetrathiafulvalene derivatives is described. The Suzuki reaction of 3,6-dichloropyridazine-fused tetrathiafulvalenes with phenyl boronic acid or biphenyl boronic acid gave a series of novel T-shaped organic π -conjugates. The electronic properties of the conjugates were studied experimentally by the combination of cyclic voltammetry and UV-vis spectroscopy. Their HOMO and LUMO energy levels are estimated to be about -5 eV and -3.2 eV, which are the air operating stability ranges in the p-channel and n-channel field effect transistors, respectively. Only one conjugate bearing the longer alkyl chain (n = 1, $R = n-C_{18}H_{37}$) was verified to self-assemble into lamellar structures in the mesogenic phase and the best measured charge carrier mobility of its thin-film devices was $4.5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

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for the preparation of organic field-effect transistors (OFETs), due to the possibility of synthesising tailored derivatives. In recent years, the study of the TTF-based OFETs, stimulated by Bourgoin's report in 1993,⁶ has gained increasing popularity.4,7,8 The largest mobilities in TTF-based OFETs have been found for single crystals prepared from a solution of dithiophenetetrathiafulvalene (DT-TTF, $\mu_{max} = 3.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),⁹ hexamethylene tetrathiafulvalene (HM-TTF, $\mu_{max} = 10 \text{ cm}^2 \text{ V}^{-1}$ $(s^{-1})^{10}$ and dibenzotetrathiafulvalene (DB-TTF, $\mu_{max} = 1 \text{ cm}^2 \text{ V}^{-1}$ s⁻¹).¹¹ Because of the strong electron-donating property of TTF, however, its derivatives are usually degraded during operation owing to moisture and oxygen. The high energy of the orbitals implicated in the transport process is the cause of the degradation, making the material more sensitive to air and humidity,12 one of the main drawbacks of TTF for practical applications. In this respect, one effective approach is the aromatic heterocycle connected to the TTF core to decrease the energy of the HOMO orbitals, which could enhance the stability of p-type and/or n-type organic semiconductors. A few organic semiconductors have been synthesized in which the TTF core is annulated to thiophene,^{9,13,14} pyrrole,^{15,16} or pyrazine^{17,18} units and all these compounds have oxidation potentials appreciably higher than that of TTF itself. Among the heterocyclic-fused TTF donors, the dipyrazine-annulated TTF derivatives showed excellent n-type FET performances in thin films ($\mu_{\rm FET}$ = 0.64 cm² V⁻¹ s⁻¹, $I_{\rm on}/I_{\rm off}$ = ~10⁶) and the dithiophene-annulated TTF derivative exhibited good p-type FET performances in single crystals ($\mu_{\text{FET}} = 1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $I_{\text{on}}/I_{\text{off}} =$ 7×10^5). Annulation of pyrazine rings to the TTF skeleton was effective in further reducing the electron-donating property,



Scheme 1 Synthetic routes to the target compounds T3 and T5

which was also useful in enhancing the stability of the FET device to oxygen.^{13,14,17,18} Very recently, it was reported that the tetrathiafulvalene fused-naphthalene diimides exhibit relatively high hole and electron mobilities in air, and the best performing device exhibited a hole mobility of up to 0.31 cm² V⁻¹ s⁻¹.¹⁹ Taking a broad view of the previous reports, however, most of the TTF-based organic semiconductors are linear rod molecules. Recently, we introduced successfully a pyridazine ring to the TTF skeleton to synthesize a series of monopyridazine–TTF conjugates. Their HOMO energy levels suggest that the conjugates can be considered as candidates for hole (p-type) or electron (n-type) transporting organic semiconductor materials.²⁰

Taking these factors into consideration, in order to establish structure–property relationships for this family of compounds, we decided to synthesize a series of T-shaped organic π -conjugates. In this paper, we describe the successful synthesis and photophysical and electrochemical properties of the novel T-shaped organic π -conjugates **T3a–b** with three aryl rings and **T5a–d** with five aryl rings (Scheme 1). The self-assembly in the mesophase state and hole transfer properties in spin-coated thin films of some selected compounds were also investigated.

Results and discussion

Synthesis

The synthetic routes to target compounds **T3** and **T5** are summarized in Scheme 1. The new intermediates **1c** and **1d** were synthesized in 88% and 95% yields, respectively, by the reaction of bis(tetraethylammonium)-bis(1,3-dithiole-2-thione-4,5dithiol) zincate with the corresponding alkyl bromides. The cross-coupling reaction of **1a–d** with ketone **2** in neat triethyl phosphite at reflux under nitrogen gave the intermediates **3a–d** in 40–63% yields. Compounds **3a–d** reacted with hydrazine monohydrate in refluxing ethanol to give the pyridazinedione derivatives **4a–d** in good yields (>70%). The key intermediates dichloropyridazino-TTFs **5a–d** were easily synthesized starting from **4a–d** with refluxing POCl₃ in ~60% yields. Compounds **T3** and **T5** were prepared through Suzuki coupling reaction in the presence of tetrakis(triphenyl-phosphine) palladium (Pd-(PPh₃)₄) and potassium carbonate in a mixed solvent (ethanolwater–benzene = 1:1:2) in 59–77% yields. The structures of the intermediates and target compounds were fully characterized using NMR spectra, MS spectra and elemental analysis data and were shown to be in full agreement with the structures presented in Scheme 1.

Crystal structure analysis and optimized structures of T3a and T5a

The structures of T3a and T5a were further confirmed by single-crystal X-ray diffraction data. In this approach, two single crystals were successfully obtained by slowly evaporating the acetonitrile solution of T3a and the mixed solution of benzene-methylene chloride of T5a at room temperature. Single-crystal X-ray diffraction structure analysis indicated that T3a crystallizes in a monoclinic system, $P2_1/c$ space group (Table S1⁺), and T5a crystallizes in a triclinic system, $P\bar{1}$ space group (Table S2[†]). In the crystal structure of compound T3a, C18 and [1,3]dithiolo[4,5-d] pyridazine, which consist of N1, N2, C7 to C10, C17, S1 and S2 (M1), are almost coplanar with the average deviation of 0.0504 Å. The two benzene rings (C1 to C6 (M2) and C11 to C16 (M3)) possess the dihedral angles of 42.67 (9)° and 44.75 (9)° with the M1, respectively. In addition, the dihedral angle of the two benzene rings is 8.35 (2)°. It is interesting that the TTF moiety does not lie in the same plane in which the 1,3-dithiole unit in the M2 possesses a dihedral angle of 15.67 (7)° with the M4 formed by C19, C20, S3 and S4, which is different from the previously reported pyridazine-fused tetrathiafulvalenes.²⁰ A butyl on one side is almost coplanar with TTF and another one lies on the other side extending along the long molecular axis with the average deviation of 30°. In the crystal of compound T5a, the atoms N1, N2, C13, C14, C15, C16, S1 and S2 nearly lie in the same plane with the average deviation from a least-squares plane (M1) of 0.0504 Å. The dihedral angles of M1 with the neighboring benzene rings M2 (C7 to C12) and M3 (C17 to C22) are 44.02 (44)° and 38.93 (47)°, respectively, while the dihedral angles of M1 with the two terminal benzene rings are smaller with a value of 12.05 (79)° for M4 (C1 to C6) and 5.89 (80)° for M5 (C23 to C28), respectively. It should be noted that the two butyls are nearly perpendicular to the TTF moiety with *cis* style (Fig. 1a). As seen in Fig. S1,[†] in the crystal structure of T3a, the intermolecular C1-H1...S1 interactions link two molecules into a dimer with a C1-S1 distance of 3.68 (1) Å. The dimers are further linked by intermolecular C27-H27A…N1 and C26-H26B…N2 hydrogen bonds with C…N distances of 3.70 (2) Å and 3.52 (1) Å respectively, forming onedimensional chains along a direction (see ESI, Fig. S1[†]). The van der Waals forces stabilize the crystal structure. For T5a, the double intermolecular C37-H37a···S4 hydrogen bonds, with a C37-S4 distance of 3.70 (3) Å, link the molecules into dimers. The dimers are further linked by intermolecular



C21–H21···S2 interactions, with a C21–S2 distance of 3.78 (2) Å, forming one-dimensional chains along the [100] direction. In addition, the weak intermolecular C–H···N hydrogen bonding, with a C25–N2 distance of 3.88 (2) Å, links the chains into a 2-D network along (01-1) (see ESI, Fig. S1[†]).

The chemical structures of T3a and T5a were investigated with theoretical calculations based on density functional theory (DFT) for a comparison with crystal structures. The optimized structures of T3a and T5a are very similar to their single-crystal structures in which the TTF moiety is also not lying in the same plane. The two benzene rings (C1 to C6 (M2) and C11 to C16 (M3)) of compound T3a possess the same dihedral angle of 42.42° with the M1. There is a difference from the crystal structure in that the two butyls are nearly perpendicular to the TTF moiety with cis style. Much the same as T3a, all benzene rings in T5a are not in the same plane as 1,3dithiolo[4,5-d]pyridazine (M1) in which the dihedral angle of M1 with the neighboring benzene rings M2 (C7 to C12) and M3 (C17 to C22) is 39.56 $^{\circ}$, while that of M2 and M3 with the two terminal benzene rings is smaller with a value of 35.63° for M4 (C1 to C6) and M5 (C23 to C28), respectively. Two butyls are nearly perpendicular to the TTF moiety with *cis* style as in the crystal structure of T5a (Fig. 1b).

Photophysical properties and rationalization

The absorption spectra of target compounds T3 and T5 in $CHCl_3$ solution (5 × 10⁻⁵ M) are shown in Fig. 2a. Compounds T3a–T3b show a very weak and broad absorption band around 425 nm and an intense absorption band around 270 nm with a shoulder band around 320 nm, respectively. Similarly, compounds T5a–T5d also show a weak and broad absorption band





3.5

3.0

2.5

2.0 1.5

1.0 0.5

0.0

Absorbance

(a)

ТЗа

Fig. 2 (a) UV-vis spectra of compounds **T3a–b** and **T5a–d** in CHCl₃ (5×10^{-5} M). (b) Variation of the UV-vis spectra of **T5d** in CHCl₃ (5×10^{-5} M) upon successive addition of varying amounts of HCl in ethanol ($0 \rightarrow 1000$ equivalents).

around 425 nm and a very intense absorption band around 310 nm, respectively. Only the absorption bands of **T5a-T5d** in the UV region were red-shifted compared to those of **T3a-T3b** (from 270 nm to 320 nm). The bands around 425 nm are assigned to the intramolecular charge transfer (ICT) interaction between the donor (TTF) and the acceptor (pyridazine). The strong bands in the UV region are characteristic of π - π * transitions located on both the TTF and the diaryl-substituted pyridazine subunits.²¹ The bands at the lower energy region can be assigned to the HOMO-LUMO transition, and thus, the onset of these bands allows us to estimate the HOMO-LUMO gap (E_g^{opt})^{22,23} that, in all cases, is around 2.52 eV (see Table 1).

To rationalize the absorption spectra of target compounds, DFT calculations were carried out for **T3a** and **T5a** by B3LYP/ 6-31G* with the Gaussian 09 program package.²⁴ The HOMOs and LUMOs of **T3a** and **T5a** are shown in Fig. S2.[†] The calculated absorption wavelengths of **T3a** and **T5a** are 421 nm/ 2.91 eV, 297 nm/3.62 eV and 441 nm/2.82 eV, 342 nm/3.86 eV, respectively, which are slightly lower/higher but in good agreement with the experimental results (Fig. 3). The lowest-energy singlet transitions at 2.91 eV and 2.82 eV involve one-electron excitations from π -orbitals HOMO to LUMO (0.57% for **T3a**

Table 1 UV-vis absorption spectroscopy data, and E^{opt}_a, HOMO and LUMO energies obtained from cyclic voltammetry for T3 and T5

Compd.	$\lambda_{\rm max, UV}/{\rm nm}$	$\lambda_{10\%, \rm max}/\rm nm$	$E_{ m g}^{ m opt \ \it a}/ m eV$	$E^{\rm red/onset}/V$	$E^{\mathrm{ox/onset}}/\mathrm{V}$	$E^{\text{HOMO }b}/\text{eV}$	$E^{\text{LUMO }b}/\text{eV}$
T3a	422	507	2.52	-1.13	0.74	-5.09	-3.22
T3b	418	505	2.53	-1.18	0.74	-5.09	-3.17
T5a	414	501	2.55	-1.13	0.74	-5.09	-3.22
T5b	418	509	2.51	-1.15	0.72	-5.07	-3.20
T5c	422	506	2.52	-1.15	0.75	-5.10	-3.20
T5d	421	509	2.51	-1.17	0.74	-5.09	-3.18

^{*a*} Optical band gap according UV-vis absorption (onset method). $E_g^{\text{opt}} = hc/\lambda_{10\%\text{max}}$ (ref. 22 and 23). ^{*b*} Energy level of the highest occupied molecular orbital according to cyclic voltammetry. $E^{\text{HOMO}/E^{\text{LUMO}}} = [-(E^{\text{onset}} - 0.45) - 4.8]$ eV, where the value 0.45 V is for ferrocene *versus* Ag/Ag⁺ and 4.8 eV is the energy level of ferrocene below the vacuum (ref. 22 and 23).



Fig. 3 Comparison of the experimental and calculated electronic absorption spectra of T3a and T5a in chloroform with the B3LYP/6-31G* method.

and 0.69% for T5a) and LUMO + 2 (0.41% for T3a and 0.13% for T5a), suggesting that this absorption corresponds to the charge-transfer absorption from the TTF part to the diarylpyridazine part. The most intense absorptions at 282 and 342 nm are predicted to be a combination of the one-electron excitations from the localized TTF or arylpyridazine, which can be attributed to one-electron excitations from π -orbitals HOMO – 1 to LUMO + 2 (0.67% for T3a and 0.57% for T5a). Two absorption bands in the UV-vis spectrum therefore bear ICT as well as localized TTF or arylpyridazine π - π * characteristics, which is very similar to a tetrathiafulvalene-diphenyl-1,3,4-oxadiazole dyad (Fig. S2 and Table S3†).²⁵

In order to explore further the ICT characteristics of the T-shaped D-A molecules, taking **T5d** as an example, the protonation characteristic was experimentally investigated in CHCl₃ solution. Compound **T5d** has two protonation sites, namely, the two nitrogen atoms on the pyridazine. The UV-vis spectra of **T5d** dissolved in CHCl₃ with successive addition of a 9 M ethanolic solution of hydrochloride (HCl) are depicted in Fig. 2b. Upon addition of HCl, for an initial concentration of 5×10^{-5} M of **T5d**, the strong absorption band at 308 nm and the broad CT absorption band at 419 nm gradually decrease in intensity and a new absorption band around 600 nm emerges. These changes continued from 0 to 1000 equivalents. A remarkable feature is the occurrence of three quite well defined isosbestic points, at 322, 408 and 445 nm for up to

1000 equivalents added, indicating the presence of only two species in the chemical equilibria, namely compound **T5d** and a mono-protonated species [**T5d**·H⁺]. The result is different from the previously reported 2-pyridinylimidazole-fused tetrathiafulvalene where two protonation sites lie on two different cycles separately,²⁶ which could be explained with the lower pK_2 of pyridazine.

Electrochemical properties

In general, p-type organic semiconductors typically have HOMO levels between -4.9 and -5.5 eV, whereas n-type materials typically have LUMO levels between -3 and -4 eV.^{27,28} To fit the energetic scheme of the organic semiconductor materials, it is necessary to determine the energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the width of the gap between the bands of each component through electrochemistry.²⁹

The electrochemical properties of T-shaped organic conjugates T3 and T5 were studied by cyclic voltammetry (CV) in benzonitrile. All compounds exhibited two reversible singleelectron oxidation waves at about 0.80 and 1.11 V. The first oxidation should be attributed to the bis(thioether)-substituted half-unit, while the second arises from the pyridazine-substituted half-unit. Moreover, the compounds showed a quasireversible reduction process at about -0.89 V, which can be assigned to one-electron reduction of the pyridazine unit (Fig. 4 and Fig. S3[†]).³⁰ The redox properties of the target compounds are similar to those of other similar TTF-fused D-A ensembles.³¹ In comparison to TTF ($E_{1/2}^1 = 0.34$ V, $E_{1/2}^2 =$ 0.73 V),³² the oxidation potentials of TTF units are positively shifted by 360-480 mV owing to the annulation of the electron-withdrawing pyridazine ring. Moreover, all compounds displayed very similar oxidation and reduction potentials, suggesting that the length of alkyl chains does not appreciably influence the redox processes. Interestingly, a unique cyclic voltammogram was observed in the case of compound T5b whose redox wave is broadened and the peak current is lowered because of an aggregation phenomenon in concentrated solutions (Fig. 4a).³³ The partial intramolecular charge transfer from the TTF unit to the pyridazine moiety decreases the electron density of the TTF ring; as a consequence, these systems are expected to be more stable to oxygen exposure.



Fig. 4 Cyclic voltammograms for oxidation (a) and reduction (b) of compounds **T5a** and **T5b** in benzonitrile (1 mM, scanning rate 100 mV s⁻¹) with platinum wires as working and counter electrodes, respectively, Ag/AgCl as a reference electrode, and *n*-Bu₄NPF₆ (0.1 M) as a supporting electrolyte.

Their HOMO levels were estimated from the onset of oxidation potentials to be between -5.07 and -5.10 eV and the LUMO levels were estimated from the onset of reduction potentials to be between -3.17 and -3.22 eV (Table 1). Clearly, all compounds provide low HOMO and LUMO levels, which suggest that the target organic π -conjugates are promising hole or electron transporting organic materials.

Electron donating properties

Taking advantage of the electron donating abilities of TTF, we carried out preliminary complexation experiments with different acceptors. However, the typical acceptors 7,7,8,8-tetracyanoethylene-*p*-quinodimethane (TCNQ) and 2,3-dichloro-5,6dicyano-*p*-benzoquinone (DDQ) were found to show no significant complexation ability with **T5d**, according to UV-vis experiments in CHCl₃. In contrast, addition of 2,3,5,6-tetrafluoro-7,7, 8,8-tetracyanoquinodimethane (F₄TCNQ), a strong electron acceptor, to a CHCl₃ solution of **T5d** (5×10^{-5} M) resulted in dramatic changes in UV-vis spectra. The UV-vis spectra of **T5d** dissolved in CHCl₃ with successive addition of F₄TCNQ are depicted in Fig. 5. Upon addition of F₄TCNQ, three new



Fig. 5 Absorption spectra of T5d (5 \times 10⁻⁵ M) in CHCl₃ after addition of different equiv. of F₄TCNQ (0 \rightarrow 20 equivalents).

absorption bands at 585, 763 and 867 nm emerged. Two new bands at 763 and 867 nm would be unambiguously assigned to the intramolecular transition of the F_4TCNQ^{+-} anion radical,³⁴ in which the band at 862 nm is likely mixed with the CT component of the complex of **T5d** with F_4TCNQ . The broad band around 585 nm could be assigned to intramolecular transitions of the radical cation, TTF^{++} ; because of that, the transitions of the charge transfer (CT) complex between TTF^{++} and F_4TCNQ^{+-} generally appear in the NIR region. In the present case, this band appeared in lower energy regions (587 nm) than those of other TTF derivatives (470–480 nm) probably due to the expansion of the conjugated system.^{34,35} Clearly, the donating ability is in agreement with the results obtained from the CV experiments.

Self-assembly

Controlled self-assembly by molecular design is a challenging topic for interdisciplinary research in the fields of chemistry, biology, and materials science because it provides spontaneous nanostructures with well-defined morphology, which plays an influential role in determining the properties of organic nanostructures.³⁶ First, we investigated the thermal phase behavior of compounds T3 and T5 by means of differential scanning calorimetry (DSC) and polarized-light optical microscopy (POM). Only one conjugate T5b bearing the longer alkyl chain (n = 1, R = n-C₁₈H₃₇) exhibited a mesogenic phase, which showed two endothermic peaks in the heating as well as in the cooling cycle (Fig. 6a). T5b exhibits a liquid crystalline phase at a melting state (123.9 °C), which was transformed to an isotropic phase at 148.2 °C. On slow cooling of T5b from the isotropic liquid to liquid crystalline phase, a natural schlieren-like texture was observed at 130 °C by POM experiments, which was transformed to a crystalline phase during cooling (Fig. 6b). The DSC curves together with optical texture preliminarily confirmed the presence of a lamellar mesophase. To investigate the molecular packing structure of T5b, we performed a small-angle X-ray scattering (SAXS) experiment after cooling to 130 °C (Fig. 6c). As seen in Fig. 6c, compound T5b has







Fig. 6 (a) DSC traces recorded during the second heating and the second cooling scan, (b) optical polarized micrographs (40x) of the texture exhibited by a lamellar phase at 130 °C, (c) X-ray diffraction patterns plotted against $q = 4\pi \sin \theta/\lambda$ measured after cooling to 130 °C, and (d) the proposed molecular arrangement in the liquid crystal of **T5b**.

a layered structure with d-spacings of 4.61, 1.52, 1.15, 0.92, 0.76 and 0.65 nm, which agreed well with (100), (300), (400), (500), (600) and (700) reflections of a lamellar packing structure. The *d*-spacing of 4.61 corresponds roughly to the molecular length extended along its long molecular axis, suggesting that the rod segments within the layers are parallel to the layer planes and are face to face stacked to each other by π - π interactions and the coil segments interdigitate with each other through hydrophobic interaction to fill the spaces between two TTF segments. Notably, compound T5b exhibits an additional sharp reflection at a d-spacing of 1.57 nm and another reflection hid likely in a broad peak at about 8.23 nm, which might be associated with the distance between two TTF segments. Two additional sharp reflections suggest that the TTF segments in T5b organize into sublayers with a thickness of 1.57 nm within a layer (Fig. 6d). The existence of in-plane sublayers in the self-assembly of T-shaped rod-coil molecules has been reported in the literature.³⁷

To verify the applicability of our new semiconductors to organic electronics, we have fabricated bottom-gate/bottomcontact OFETs with thin films of T3a and T5b, which were prepared by spin-coating of their solutions onto the substrates (n-octadecyltrimethoxysilane (OTS) modified SiO₂ surface). The field-effect transistors were fabricated in air with conventional techniques by using doped n-type Si as the gate electrode, Au as both the source and drain electrodes and OTS-modified SiO₂ as the dielectric layer. The OFET devices were examined in air, and the corresponding output characteristics and transfer characteristics were measured (see ESI⁺). Both thin films show typical p-type semiconducting behavior in the air. And the mobilities of T3a and T5b were 3.4 \times $10^{-6}~\text{cm}^2~\text{V}^{-1}~\text{s}^{-1}$ and $4.5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Fig. 7 shows the XRD patterns of thin films of T5b annealed at different temperatures. Weak diffraction peaks at 5.8°, 6.1°, 6.8°, 9.0°, 11.3°, 13.5°, 16.4°, 18.0°, 20.1°, 20.7°, 23.4°, 24.1°, and 24.7° were detected for thin films of T5b after annealing at 80 °C. After annealing at 100 °C, the peaks at 5.8°, 6.1°, 16.4°, 18.5°, 20.7°, 23.4°, and 24.1° disappear. After further annealing at 120 °C, the



Fig. 7 XRD patterns of thin films of T5b after annealing at 80 °C, 100 °C, 120 °C and 140 °C, respectively.

remaining peaks at 6.8°, 9.0°, 11.3°, 13.5°, 18.0°, 20.1°, and 24.7° were largely enhanced. After annealing at 140 °C, the peak intensity at 6.8° weakens, whereas other diffraction peaks still remain; but two new diffraction peaks appear at 3.6° and 4.5° with high intensity. These XRD data clearly show that molecules of **T5b** are more orderly arranged for the thin film of **T5b** after annealing until 140 °C. Taking into account that neither the substrate–semiconductor nor the semiconductor–dielectric interface was optimized, we expect a large amount of potential improvement in the electron mobility.

Experimental section

General methods

NMR spectra were recorded in CDCl₃ with a Bruker AV-300 spectrometer (300 MHz for ¹H and 75 MHz for ¹³C) and chemical shifts were referenced relative to tetramethylsilane ($\delta_{\rm H}/\delta_{\rm C}$ = 0). MALDI-TOF-MS was performed on a Shimadzu Axima CFR[™] Plus using a 1,8,9-anthracenetriol (DITH) matrix. UV-vis spectra were recorded on a Hitachi U-3010 spectrophotometer in CHCl₃ (5 \times 10⁻⁵ M). Cyclic voltammetric studies were carried out on a Potentiostat/Galvanostat 273A instrument in benzonitrile (10^{-3} M) and 0.1 M Bu₄PF₆ was used as the supporting electrolyte. The counter and working electrodes were made of Pt and glassy carbon, respectively, and Ag/AgCl was used as the reference electrode. A Perkin-Elmer Pyris Diamond differential scanning calorimeter was used to determine the thermal transitions, which were reported as the maxima and minima of their endothermic or exothermic peaks; the heating and cooling rates were controlled at 10 °C min⁻¹. An Olympus BX51-P optical polarized microscope (magnification: 40×), equipped with a Mettler FP82 hot-stage and a Mettler FP90 central processor, was used to observe the thermal transitions and to analyze the anisotropic texture. X-ray scattering measurements were performed in the transmission mode with synchrotron radiation from the 3C2 X-ray beam line at the Pohang Accelerator Laboratory, Korea. X-ray diffraction (XRD) measurements of the thin films were carried out in the reflection mode at room temperature using a 2 kW Rigaku X-ray diffraction system. Compounds 1a,³⁸ 1b,³⁹ 3b,⁴⁰ 3a, 4a and 5a,²⁰ and 2⁴¹ were synthesized according to a literature method. For the synthesis of 1c, 1d, 3c, 3d, 4b, 4c, 4d, 5b, 5c and 5d, see ESI.[†]

Typical procedure for compounds T3 and T5

A mixture of 5 (0.21 mmol), arylboronic acid (0.82 mmol), Pd(PPh₃)₄ (0.10 mmol) and K_2CO_3 (1.48 mmol) in a mixture of EtOH-H₂O-C₆H₆ = 1:1:2 (10 mL) was stirred under N₂ at 90 °C for 12 h. After cooling, the resulting mixture was dissolved in CH₂Cl₂, washed with water and dried over MgSO₄. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel using CH₂Cl₂ to give a solid.

Compound T3a. Recrystallization from CH₃CN gave an orange needle, yield 77.5%. m.p. 151–152 °C; ¹H NMR

(300 MHz, CDCl₃, 25 °C, TMS): δ = 7.92–7.89 (m, 4H, Ar), 7.56–7.47 (m, 6H, Ar), 2.81 (t, ³*J* (H,H) = 7.2 Hz, 4H, SCH₂), 1.57–1.46 (m, 4H, CH₂), 1.39–1.25 (m, 4H, CH₂), 0.91 ppm (t, ³*J* (H,H) = 7.3 Hz, 6H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ = 152.1, 140.2, 136.6, 130.2, 128.9, 127.9, 115.4, 105.2, 36.0, 31.7, 21.6, 13.5 ppm; MS (MALDI-TOF): *m*/*z* (%): 585.1 ([*M*⁺ + H], 100); elemental analysis calcd for C₂₈H₂₈N₂S₆: C 57.49, H 4.82, N 4.79; found: C 57.31, H 4.78, N 4.66.

Compound T3b. Recrystallization from acetone gave an orange powder, yield 64.9%. m.p. 99–100 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 7.92–7.88 (m, 4H, Ar), 7.59–7.54 (m, 6H, Ar), 2.80 (t, ³*J* (H,H) = 7.2 Hz, 4H, SCH₂), 1.43–1.36 (m, 4H, CH₂), 1.32–1.25 (m, 4H, CH₂), 1.25–1.24 (m, 56H, CH₂), 0.91 ppm (t, ³*J* (H,H) = 7.3 Hz, 6H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ = 152.2, 140.2, 136.6, 130.2, 128.9, 128.0, 127.8, 115.6, 105.2, 36.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.1, 28.5, 22.7, 14.1 ppm; MS (MALDI-TOF): *m*/*z* (%): 977.8 ([*M*⁺ + H], 100); elemental analysis calcd for C₅₆H₈₄N₂S₆: C 68.80, H 8.66, N 2.87; found: C 69.00, H 8.69, N 2.76.

Compound T5a. Recrystallization from $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN}$ gave a yellow powder, yield 73.7%. m.p. 216–217 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 8.02 (d, ³J (H,H) = 8.13 Hz, 4H, Ar), 7.81 (d, ³J (H,H) = 8.28 Hz, 4H, Ar), 7.69 (d, ³J (H,H) = 8.13 Hz, 4H, Ar), 7.53–7.48 (m, 4H, Ar), 7.44–7.39 (m, 2H, Ar), 2.82 (t, ³J (H,H) = 7.3 Hz, 4H, SCH₂), 1.65–1.56 (m, 4H, CH₂), 1.49–1.37 (m, 4H, CH₂), 0.92 ppm (t, ³J (H,H) = 7.23 Hz, 6H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ = 51.8, 143.1, 140.3, 140.2, 128.9, 128.4, 127.9, 127.6, 127.2, 111.9, 105.2, 36.1, 31.7, 21.6, 13.6 ppm; MS (MALDI-TOF): m/z (%): 736.2 ([M^+], 100); elemental analysis calcd for C₄₀H₃₆N₂S₆: C 65.18, H 4.92, N 3.80; found: C 65.22, H 4.98, N 4.02.

Compound T5b. Recrystallization from CH₂Cl₂-hexane gave a yellow powder, yield 59.3%. m.p. 158–159 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 8.0 2 (d, ³*J* (H,H) = 8.13 Hz, 4H, Ar), 7.81 (d, ³*J* (H,H) = 8.22 Hz, 4H, Ar), 7.69 (d, ³*J* (H,H) = 7.74 Hz, 4H, Ar), 7.53–7.48 (m, 4H, Ar), 7.42–7.39 (m, 2H, Ar), 2.81 (t, ³*J* (H,H) = 7.23 Hz, 4H, SCH2), 1.66–1.56 (m, 4H, CH₂), 1.40–1.23 (m, 60H, CH₂), 0.87 ppm (t, ³*J* (H,H) = 6.36 Hz, 6H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ = 151.7, 143.1, 140.2, 135.3, 128.9, 128.4, 127.9, 127.6, 127.2, 115.7, 105.2, 36.4, 31.9, 29.7, 29.6, 29.5, 29.3, 29.1, 28.5, 22.7, 14.1 ppm; MS (MALDI-TOF): *m*/*z* (%): 1130.0 ([*M*⁺ + H], 100); elemental analysis calcd for C₆₈H₉₂N₂S₆: C 72.29, H 8.21, N 2.48; found: C 72.45, H 8.50, N 2.55.

Compound T5c. Recrystallization from acetone gave an orange powder, yield 61.9%. m.p. 112–113 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 8.02 (d, ³*J* (H,H) = 8.25 Hz, 4H, Ar), 7.80 (d, ³*J* (H,H) = 8.19 Hz, 4H, Ar), 7.69 (d, ³*J* (H,H) = 7.11 Hz, 4H, Ar), 7.52–7.47 (m, 4H, Ar), 7.43–7.36 (m, 2H, Ar), 2.82 (d, ³*J* (H,H) = 6.06 Hz, 4H, SCH₂), 1.73 (m, 4H, CH₂), 1.61–1.55 (m, 4H, CH₂), 1.36–1.34 (m, 6H, CH₂), 1.25–1.23 (m, 52H, CH₂), 0.89 ppm (t, ³*J* (H,H) = 6.51 Hz, 12H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ = 151.7, 143.0, 140.2, 140.1, 135.3, 128.9, 128.4, 128.0, 127.8, 127.6, 127.1, 41.1, 38.2, 32.8, 31.9, 29.9, 29.8, 29.7, 29.6, 29.4, 26.5, 22.7, 14.1 ppm; MS (MALDITOF): *m/z* (%): 1185.5 ([*M*⁺ + H]); elemental analysis calcd for

 $C_{72}H_{100}N_2S_6{:}$ C 72.92, H 8.50, N 2.36; found: C 72.65, H 8.33, N 2.60.

Compound T5d. Recrystallization from acetone gave an orange powder, yield 59.0%. m.p. 114–115 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): $\delta = 8.02$ (d, ³*J* (H,H) = 8.13 Hz, 4H, Ar), 7.80 (d, ³*J* (H,H) = 8.01 Hz, 4H, Ar), 7.69 (d, ³*J* (H,H) = 7.17 Hz, 4H, Ar), 7.52–7.47 (m, 4H, Ar), 7.43–7.36 (m, 2H, Ar), 2.82 (d, ³*J* (H,H) = 5.91 Hz, 4H, SCH₂), 1.63–1.57 (m, 8H, CH₂), 1.35–1.34 (m, 6H, CH₂), 1.23 (m, 68H, CH₂), 0.89 ppm (t, ³*J* (H, H) = 6.68 Hz, 12H, CH₃); ¹³C NMR (75 MHz, CDCl₃): $\delta = 151.7$, 143.0, 140.2, 140.1, 135.3, 18.9, 128.4, 128.0, 127.8, 127.5, 127.2, 41.1, 38.2, 32.8, 31.9, 29.9, 29.7, 29.4, 26.5, 22.7, 14.1 ppm; MS (MALDI-TOF): *m*/*z* (%): 1298.0 ([*M*⁺ + H], 100); elemental analysis calcd for C₈₀H₁₁₆N₂S₆: C 74.02, H 9.01, N 2.16; found: C 73.75, H 9.12, N 1.98.

Conclusions

In summary, we have synthesized a series of T-shaped π -conjugates from a new building block, dichloropyridazine-fused TTFs, through the Suzuki reaction and they were fully characterized. Spectroscopic and electrochemical studies revealed that the pyridazine unit greatly facilitates electronic communication between the TTF moiety and the acceptor unit, thus leading to intramolecular charge transfer, and the protonation of the pyridazine moiety showed an ICT band of the protonated species. The HOMO and LUMO energy levels of target compounds are estimated to be close to -5 eV and -3.2 eV, which are the air operating stability ranges in the p-channel and n-channel field effect transistors, respectively, and the best measured charge carrier mobility of the spin-coated film device of T5b bearing the longer alkyl chain (n = 1, R = *n*-C₁₈H₃₇), which shows a lamellar mesophase, was 4.5 \times 10⁻⁵ cm² V⁻¹ s⁻¹. Further structural modification and improvement of the mobility of the T-shaped conjugates are underway in our laboratories.

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