Supporting Information

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

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Synthesis of intermediates

Typical procedure for compounds 1: A mixture of tetrabutylammonium bis(2-thioxo-1,3-dithiole-4,5-dithio-late) zincate (1.31g, 1.81mmol) and the corresponding alkyl bromide[1,2] (9.05mmol) in CH_3CN (60mL) was refluxed overnight. After cooling, the solution was evaporated in vacuo to dryness. The residue was purified by column chromatography on silica gel using CH_2Cl_2/petroleum ether (60-90ºC) (v/v, 1:5) as the eluent to give **1**.

Compound 1c. A yellow oil, yield 87.8%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.86 (d, ^3J (H,H) = 6.15 Hz, 4H, SCH_2), 1.65-1.57 (m, 4H, CH_2), 1.36-1.27 (m, 60H, CH_2), 0.93 ppm (t, ^3J (H,H) = 7.5 Hz, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.2, 136.4, 41.5, 36.6, 39.4, 38.1, 32.8, 32.5, 31.9, 29.9, 29.8, 29.7, 29.68, 29.66, 29.61, 29.4, 26.5, 26.4, 22.7, 14.1 ppm; MS (MALDI-TOF): *m/z* (%): 759.0 ([M^+], 100).

Compound 1d. A yellow oil, yield: 95.1%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.86 (d, ^3J (H,H) = 6.15 Hz, 4H, SCH_2), 1.65-1.57 (m, 4H, CH_2), 1.36-1.26 (m, 74H, CH_2), 0.93 ppm (t, ^3J (H,H) = 7.5 Hz, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.2, 136.4, 41.5, 36.6, 39.4, 38.1, 32.8, 32.5, 31.9, 29.9, 29.8, 29.7, 29.68, 29.66, 29.61, 29.4, 26.5, 26.6, 22.7, 14.1 ppm; MS (MALDI-TOF): *m/z* (%): 870.9 ([M^+], 100).

Typical procedure for compounds 3: A mixture of **1** (3.17mmol) and **2** (0.62g, 2.64 mmol) in $P(OEt)_3$ (15mL) was stirred at 130 ºC for 30 min under N_2. After cooling, the solution was evaporated in vacuo to dryness. The residue was purified by column chromatography on silica gel using DCM/petroleum ether (v/v, 1:4) as the eluent to give **3.**

Compound 3c. A dark red oil, yield 39.6%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 6H, $COOCH_3$), 2.82 (d, ^3J (H,H) = 6.0 Hz, 4H, SCH_2), 1.60-1.27 (m, 66H, CH_2), 0.89 ppm (t, ^3J (H,H) = 6.51 Hz, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.9, 131.9, 128.1, 121.3, 112.7, 107.6, 53.3, 41.1, 38.2, 32.8, 31.9, 29.9, 29.7, 29.6, 29.4, 26.5, 22.7, 14.1 ppm; MS (MALDI-TOF): *m/z*

(%) 943.9 ([*M*$^+$], 100).

Compound 3d. A dark-red oil, yield 42.6%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 6H, $COOCH_3$), 2.80 (d, ^3J (H, H) = 6.0 Hz, 4H, SCH_2), 1.60-1.27 (m, 82H, CH_2), 0.87 ppm (t, ^3J (H,H) = 6.51 Hz, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.9, 131.9, 128.1, 121.0, 112.8, 107.6, 53.2, 41.1, 38.1, 32.8, 31.9, 29.9, 29.7, 29.6, 29.4, 26.5, 22.7, 14.1 ppm; MS (MALDI-TOF): *m/z* (%): 1056.2 ([*M*$^+$], 100).

Typical procedure for compounds 4: A mixture of **3** (0.31mmol) and hydrazine hydrate (5mL) in EtOH (15mL) and THF (15mL) was refluxed overnight. After cooling, the precipitate was filtered off and was washed with water for **4b.** After cooling, the solution was evaporated in vacuo to dryness. The residue was dissolved in CH_2Cl_2 and washed with water, dried over $MgSO_4$ and purified by column chromatography on silica gel using CH_2Cl_2/CH_3OH (v/v, 10:1) as the eluent for **4c** and **4d.**

Compound 4b. A red solid, yield 67.3%. m.p. 116-118 ºC. MS (MALDI-TOF): *m/z* (%): 856.4 ([*M*$^+$], 100). Structure of **4b** is impossible to be fully characterized owing to its extreme insolubility.

Compound 4c. A viscous red oil, yield 74.4 %. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.83 (d, ^3J (H,H) = 5.55 Hz, 4H, SCH_2), 1.60-1.56 (m, 4H, CH_2), 1.37-1.27 (m, 62H, CH_2), 0.89 ppm (t, ^3J (H,H) = 6.51 Hz, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.9, 138.2, 128.1, 115.7, 105.6, 41.2, 38.2, 32.9, 32.0, 30.1, 29.8, 29.7, 29.5, 26.6, 22.7, 14.2 ppm; MS (MALDI-TOF): *m/z* (%): 912.0 ([*M*$^+$], 100).

Compound 4d. A viscous red oil, yield 71.1%. ^{1}H NMR (300 MHz, CDCl3): δ = 2.83 (d, ^3J (H,H) = 5.55 Hz, 4H, SCH_2), 1.61-1.59 (m, 4H, CH_2), 1.42-1.26 (m, 78H, CH_2), 0.87 ppm (t, ^3J (H,H) = 6.52 Hz, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.9, 138.2, 128.1, 115.7, 105.6, 41.2, 38.2, 32.0, 30.1, 29.8, 29.79, 29.76, 29.5, 26.6, 22.7, 14.2 ppm; MS (MALDI-TOF): *m/z* (%): 1056.2 ([*M*$^+$], 100).

Typical procedure for compound 5: Compound **4** (0.26mmol) was refluxed overnight in neat $POCl_3$ (10mL). The mixture was cooled, and the excess $POCl_3$ was evaporated to dryness under reduced pressure. The crude product was washed using CH_3OH for **5b** or silica gel using CH_2Cl_2/petroleum ether (60-90ºC) (v/v, 1:5) as the eluent for **5c** and **5d.**

Compound 5b. A cherry like red solid, yield 83.4%. m.p. 80-82 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.83 (d, ^3J (H,H) = 7.29 Hz, 4H, SCH_2), 1.61-1.45 (m, 4H, CH_2), 1.45-1.25 (m, 56H, CH_2), 0.88 ppm (t, ^3J (H, H) = 6.90 Hz, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.6, 142.4, 128.1, 120.2, 100.8, 36.5, 31.9, 29.7, 29.6, 29.5, 29.4, 29.1, 28.5, 22.7, 14.2 ppm; MS (MALDI-TOF): *m/z* (%): 893.6 ([*M*$^+$], 100).

Compound 5c. A viscous dark-red oil, yield: 70.0%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.83 (d, ^3J (H,H) = 6.06 Hz, 4H, SCH_2), 1.60-1.56 (m, 4H, CH_2), 1.37-1.27 (m, 62H, CH_2), 0.89 ppm (t, ^3J (H, H) = 6.51 Hz, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.6, 142.3, 128.3, 120.0, 100.6, 41.3, 38.2, 32.8, 31.9, 29.9, 29.7, 29.4, 26.5, 22.7, 14.1 ppm; MS (MALDI-TOF): *m/z* (%): 949.5 ([*M*$^+$+H], 100).

Compound 5d. A viscous dark-red oil, yield: 73.2%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.83 (d, ^3J

(H,H) = 6.06 Hz, 4H, SCH_2), 1.60-1.56 (m, 4H, CH_2), 1.37-1.27 (m, 78H, CH_2), 0.89 ppm (t, ^3J (H,H) = 6.68 Hz, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.6, 142.4, 128.3, 119.9, 104.1, 41.3, 38.2, 32.8, 31.9, 29.9, 29.7, 29.4, 26.5, 22.7, 14.1 ppm; MS (MALDI-TOF): *m/z* (%): 1061.0 ([M^++H], 100).

Tables

Table S1. Crystal data and structure refinements for compound **T3a.**

Empirical formula	$C_{28}H_{28}N_2S_6$
Formula weight	584.88
Temperature	273 (2) K
Wavelength	0.71073 A
Crystal system	monoclinic
Space group	P 2_1/c
a (Å)	14.734 (3)
b (Å)	8.0689 (16)
c (Å)	25.063 (5)
α (°)	90
β (°)	105.52 (3)
γ (°)	90
V (Å^3)	2871.0 (10)
Z	4
$D_{calc.}$(g cm^{-3})	1.353
Abs coeff. (mm^{-1})	0.50
F(000)	1224
R(int)	0.069
GOOF on F^2	1.026
Final R indices [I>2sigma(I)]	^{a}R1 = 0.0562, ^{b}R_w = 0.1160
R indices (all data)	^{a}R1 = 0.1132, ^{b}R_w = 0.1396

^{a} R1 = $||F_o| - |F_c||/|F_o|$. ^{b} $R_w = [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$.

Table S2. Crystal data and structure refinements for compound **T5a.**

Empirical formula	$C_{40}H_{36}N_2S_6$
Formula weight	737.07
Temperature	291(2) K
Wavelength	0.71073 A
Crystal system	triclinic
Space group	P-1
a (Å)	9.0851 (18)
b (Å)	13.860 (3)

c (Å)	16.244 (3)
α (°)	105.68 (3)
β (°)	106.12 (3)
γ (°)	99.11
V (Å^3)	1830.8 (6)
Z	2
$D_{calc.}$(g cm^{-3})	1.337
Abs coeff. (mm^{-1})	0.406
F(000)	772
R(int)	0.1352
GOOF on F^2	1.424
Final R indices [I>2sigma(I)]	^{a}R1 = 0.1892, ^{b}R$_w$ = 0.5106
R indices (all data)	^{a}R1 = 0.3287, ^{b}R$_w$ = 0.5530

^{a} $R1 = ||F_o| - |F_c||/|F_o|$. ^{b} $R_w = [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$.

Table S3. The excitation energies (eV), wavelengths (nm), oscillator strengths (*f*) for low-lying singlet excited states of **T3a** and **T5a** calculated in CH_2Cl_2 at TD-B3LYP/6-31G(d) level.

Molecule	Cal. (nm / eV)	Composition	*f*
T3a	426 / 2.91	H→L (0.57 %)	0.0390
		H→L+2 (0.41 %)	
	297 / 4.17	H-1→L (0.67 %)	0.6653
T5a	441 / 2.81	H→L (0.69 %)	0.0767
		H→L+2 (0.13 %)	
	342 / 3.62	H-1→L (0.57 %)	1.0498

H denotes HOMO and L denotes LUMO

Figures

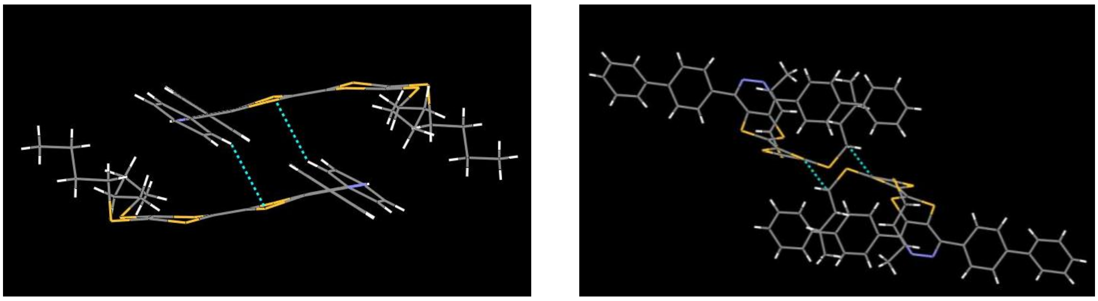
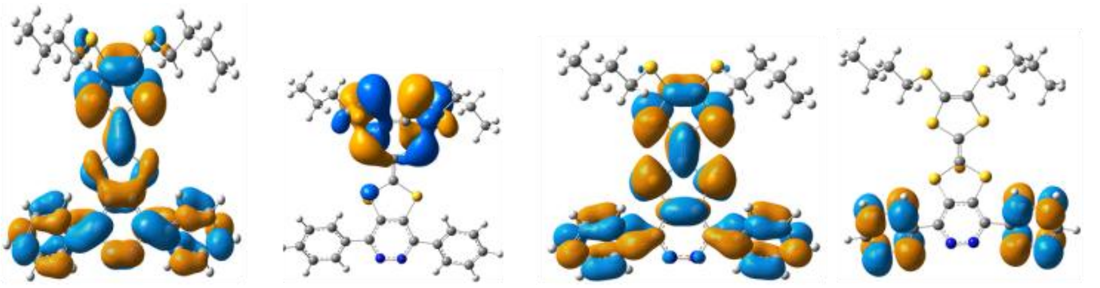
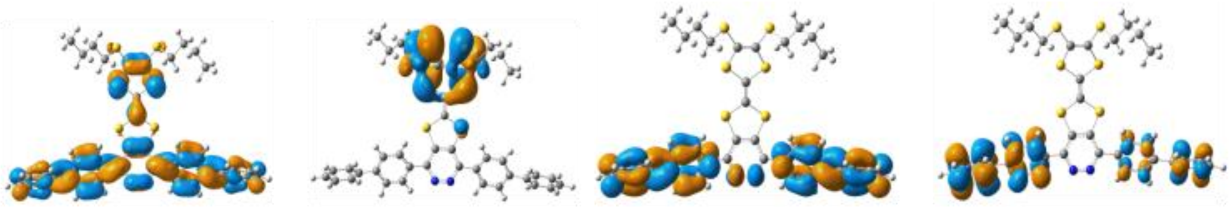


Figure S1. View of the crystal packing arrangement of **T3a** (left) and **T5a** (right).



T3a HOMO (-5.84eV) **T3a** HOMO-1 (-7.12eV) **T3a** LUMO (-2.41eV) **T3a** LUMO+2 (-1.95eV)



T5a HOMO (-5.85eV) **T5a** HOMO-1 (-6.71eV) **T5a** LUMO (-2.57eV) **T5a** LUMO+2 (-5.84eV)

Figure S2. Frontier molecular orbitals involved in the main excitation transitions of **T3a** and **T5a** in $CHCl_3$ are calculated using B3LYP with the 6-31G(d) basis set with an isodensity surface of 0.02.

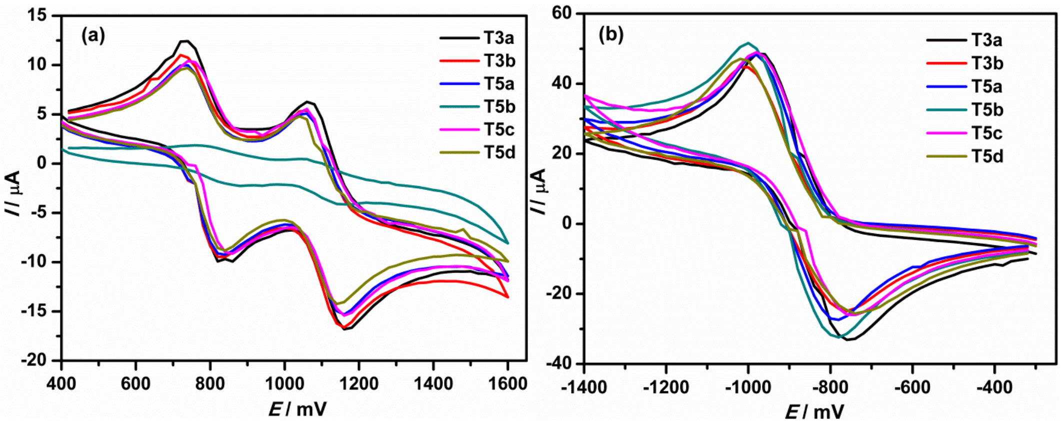


Figure S3. Cyclic voltammograms for oxidation (a) and reduction (b) of compounds **T3** and **T5** in benzonitrile (1 mM, scanning rate 100 mV/s) with platinum wires as working and counter electrodes, respectively, Ag/AgCl as a reference electrode, and *n*-Bu_4NPF_6 (0.1 M) as a supporting electrolyte.

Fabrication and Characterization of OFETs:

Bottom-gate/bottom-contact OFETs were fabricated with conventional techniques. Briefly, a heavily doped *n*-type Si wafer and a layer of dry oxidized SiO_2 (300 nm, with roughness lower than 0.1 nm and capacitance of 11 nF·cm^{-2}) were used as a gate electrode and gate dielectric layer, respectively. The drain-source (*D*-*S*) gold contacts were fabricated by photo-lithography. The channel length and width are 50 μm and 1440 μm, respectively. The substrates were cleaned in water, deionized water, alcohol, and rinsed in acetone. Then, the surface was modified with *n*-octadecyltrimethoxysilane (OTS). Compounds **T3a** and **T5b** were dissolved in $CHCl_3$ (about 10 mg/mL) and spin-coated on above substrate at 2000 rpm. The annealing processes were carried in vacuum condition for 1.0 hr at each temperature.

The mobility of the OFETs in the saturation region was extracted from the following equation:

$$I_{DS} = \frac{W}{2L}\mu C_i\left(V_{GS} - V_{th}\right)^2$$

where I_{DS} is the drain electrode collected current; L and W are the channel length and width, respectively; μ is the mobility of the device; C_i is the capacitance per unit area of the gate dielectric layer; V_{GS} is the gate voltage, and V_{th} is the threshold voltage. The V_{th} of the device was determined by extrapolating the $(I_{\mathrm{DS,sat}})^{1/2}$ vs. V_{GS} plot to $I_{\mathrm{DS}} = 0$.

References:

[1] Steve R. Bull; Liam C. Palmer; Nathaniel J. Fry; Megan A. Greenfield; Benjamin W. Messmore; Thomas J. Meade; and Samuel I. Stupp. *J. Am. Chem. Soc.* **2008**, *130*, 2742-2743.

[2] Xugang Guo and Mark D. Watson. *Org. Lett.* **2008**, *10*, 5333-5336.