Electronic Supplementary Material (ESI)

Quinoidal thioalkyl-substituted bithiophene small molecule semiconductor for n-type organic field effect transistors

Vellaichamy Joseph,^{‡^a} Chih-Hsin Yu,^{‡^b} Chia-Chi Lin,^{‡^b} Wei-Chieh Lien,^a Hsin-Chia Tsai,^a Cheng-Shiun Chen,^a Alfonsina Abat Amelenan Torimtubun,^b Arulmozhi Velusamy,^a Ping-Yu Huang,^a Gene-Hsiang Lee,^c Shueh-Lin Yau,^a Shih-Hung Tung,^d Takeo Minari,^e Cheng-Liang Liu^{*f} and Ming-Chou Chen^{*a}

^a Department of Chemistry and Research Center of New Generation Light Driven Photovoltaic Module, National Central University, Taoyuan 32001, Taiwan. E-mail: mcchen@ncu.edu.tw

^b Department of Chemical and Materials Engineering, National Central University, Taoyuan 32001, Taiwan.

^c Instrument Center, National Taiwan University, Taipei 10617, Taiwan

^d Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

^e Center for Sensor and Actuator (CFSN), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, 305-0044, Japan

^f Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan. E-mail: liucl@ntu.edu.tw

‡ These authors contributed equally to this work.

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Materials and Characterization

All the chemical reagents were procured from Aldrich, Alfa and TCI Chemical Co. and used as received without any further purification. Solvents for reactions (toluene and THF) were distilled under nitrogen atmosphere by conventional distillation method using sodium/benzophenone, and halogenated solvents were distilled using calcium hydride as drying agent. Silica gel (230 mesh size) was used as stationary phase for column chromatography. ¹H NMR and ¹³C NMR were recorded on a Bruker instrument at 500 MHz and 125 MHz respectively. Deuterated chloroform (CDCl₃) was used as solvent and the chemical shifts were calibrated using the residual peak of CDCl₃ at δ 7.26 for ¹H and δ 77.0 for ¹³C NMR spectra respectively. UV-Vis absorption spectra were recorded at room temperature in a quartz cuvette using JASCO V-600 UV-Vis spectrophotometer. Differential scanning calorimetry (DSC) was carried out under a nitrogen atmosphere on a Mettler DSC 822 instrument (scanning rate of 10 °C min⁻¹). Thermogravimetric analysis (TGA) was performed using a Perkin Elmer TGA-7 instrument under nitrogen as a carrier gas and the reported decomposition temperatures indicate the temperature corresponding to 5% weight loss. Differential pulse voltammetry experiments were performed using a CHI621C Electrochemical Analyzer (CH Instruments) with a conventional three-electrode system (a platinum disk working electrode, an auxiliary platinum wire electrode, and a non-aqueous Ag reference electrode) and supporting electrolyte of 0.1 Μ tetrabutylammoniumhexafluorophosphate (TBAPF₆) in o-dichlorobenzene solution. All electrochemical potentials were calibrated to an Fc/Fc⁺ internal standard (at 0.6 V). The surface morphologies of the solution-sheared **TSBTQ** crystalline thin films were measured by polarized optical microscopy (POM; Leica 2700M) and atomic force microscopy (tapping mode AFM; Seiko SPA400). The microstructures of the thin films of **TSBTO** compounds were investigated by grazing incident X-ray diffraction (GIXRD) at the B13A1 and B17A1 beamline of National Synchrotron Radiation Research Center (NSRRC, Taiwan)



Scheme S1. Synthetic route for the target TSBTQ compounds.

General procedure for the synthesis of 4

n-BuLi was added to 3,4-bis(alkylthio)thiophene (**3a-3b**) in THF under nitrogen atmosphere for 30 minutes at 0 °C. Then $ZnCl_2$ was added over 20 minutes at 0 °C. Further, temperature was lowered to -78 °C and CuCl₂ was added and reaction was allowed for 12 h at room temperature. After completion of reaction, the reaction mixture was washed with water and extracted with diethyl ether. The collected organic layer was dried over sodium sulphate and evaporated in rotary evaporator under reduced pressure. The concentrated compound was purified by column chromatography using hexane/DCM (19:1) as eluent.

Synthesis of 4a: This compound is obtained as colorless liquid. Yield 50%. ¹H NMR (500 MHz, CDCl₃) δ 6.98 (s, 2 H), 2.94 (t, *J* = 7.3 Hz, 4 H), 2.72 (t, *J* = 7.3 Hz, 4 H), 1.73-1.70 (m, 4 H), 1.56-1.44 (m, 8 H), 1.42-1.33 (m, 8 H), 1.32-1.22 (m, 12 H), 0.92 (t, *J* = 6.8 Hz, 6 H), 0.87 (t, *J* = 6.4 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 138.45, 137.93, 130.86, 119.26, 36.11, 33.62, 31.42, 31.38, 29.45, 28.73, 28.69, 28.39, 22.55, 140.01. HRMS (*m*/*z* FAB+) calcd. for C₃₂H₅₄S₆: 630.2550. Found: 630.2551.

Synthesis of 4b: This compound is obtained as color solid. Yield 57%. ¹H NMR (500 MHz, CDCl₃) δ 6.98 (s, 2H), 2.93 (t, *J* = 7.3 Hz, 4H), 2.71 (t, *J* = 7.3 Hz, 4H), 1.73-1.70 (m, 4H),

1.47-1.43 (m, 8H), 1.26-1.98 (m, 52H), 0.88 (t, J = 3.5 Hz, 12H). ¹³C NMR (125 MHz, CDCl₃): δ 138.47, 137.94, 130.79, 119.16, 36.09, 33.59, 31.92, 29.70, 29.58, 29.48, 29.35, 29.26, 29.20, 29.05, 28.77, 28.73, 27.12, 14.12. HRMS (m/z FAB+) calcd. for C₄₈H₈₇S₆: 855.5132. Found: 855.5132.

General procedure for the preparation of 5

NBS was added to 3,3',4,4'-tetrakis(alkythio)thiophenes (**4a-4b**) dissolved in DCM at 0 °C. The reaction mixture was warmed to 30 °C for 12 h. After completion of reaction, water was added to the reaction mixture and extracted with diethyl ether. Further, the organic layer is concentrated and purified by column chromatography using hexane as eluent.

Synthesis of 5a: This compounds is obtained as colorless solid. Yield 74%. ¹H NMR (500 MHz, CDCl₃) δ 2.89 (t, J = 7.3 Hz, 4 H), 2.78 (t, J = 7.3 Hz, 4 H), 1.57-1.42 (m, 12 H), 1.29-1.22 (m, 20 H), 0.89 (t, J = 6.8 Hz, 12 H). ¹³C NMR (125 MHz, CDCl₃): δ 137.13, 136.46, 135.12, 120.85, 36.90, 35.99, 31.43, 31.37, 29.53, 29.34, 28.44, 28.37, 22.56, 14.04. HRMS (m/z FAB⁺) calcd. for C₃₂H₅₂S₆Br₂: 788.0740. Found: 788.0740.

Synthesis of 5b: This compound is obtained as pale-yellow color solid. Yield 86%. ¹H NMR (500 MHz, CDCl₃) δ 2.89 (t, *J* = 7.3 Hz, 4 H), 2.78 (t, *J* = 7.4 Hz, 4 H), 1.56-1.54 (m, 4 H), 1.49-1.46 (m, 4 H) 1.42-1.22 (m, 56 H), 0.87 (t, *J* = 6.6 Hz, 12 H). ¹³C NMR (125 MHz, CDCl₃): δ 137.14, 136.43, 135.07, 120.86, 36.89, 35.99, 31.92, 29.59, 29.35, 29.25, 28.79, 28.71, 22.69, 14.13. HRMS (*m*/*z* FAB+) calcd. for C₄₈H₈₄S₄B_{r2}: 1010.3264. Found: 1010.3263.

Identification code	ic18304
Empirical formula	C38 H52 N4 S6
Formula weight	757.19
Temperature	220(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 36.4760(9) Å
	$\alpha = 90^{\circ}.$
	b = 7.83102(2) Å
	$\beta = 111.6400(8)^{\circ}$
	c = 15.4491(4) Å
	$\gamma = 90^{\circ}.$
Volume	4101.91(18) Å ³
Ζ	4
Density (calculated)	1.226 mg/m ³
Absorption coefficient	3.312 mm ⁻¹
F(000)	1616
Crystal size	0.344 x 0.043 x 0.013 mm ³
Theta range for data collection	5.218 to 69.975°.
Index ranges	-44<=h<=44, -8<=k<=9, -18<=l<=18
Reflections collected	12806
Independent reflections	3862 [R(int) = 0.0215]
Completeness to theta = 67.679°	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7533 and 0.5498
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3862 / 0 / 219
Goodness-of-fit on F ²	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.1143
R indices (all data)	R1 = 0.0436, wR2 = 0.1195
Extinction coefficient	n/a
Largest diff. peak and hole	0.533 and -0.204 e.Å ⁻³
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.1143
R indices (all data)	R1 = 0.0436, wR2 = 0.1195
Extinction coefficient	n/a

 Table S1. Crystal data and structure refinement for TSBTQ-6 (1)

Largest diff. peak and hole0.533 and -0.204 e.Å⁻³

Crystallographic data (excluding structure factors) of **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1993957.





Fig. S1 DSC curve of TSBTQ-6 and TSBTQ-10.



Fig. S2 TGA curves of the TSBTQ-6 and TSBTQ-10.



Fig. S3 DFT/ B3LYP-derived molecular orbital contours and energetic LUMO and HOMO

energy level alignment of the **TSBTQs** compounds. (a, c) **TSBTQ-6** and (b, d) **TSBTQ-10**.



Fig. S4 (a) Molecular structure of **TSBTQ-6** (1) by single crystal X-ray analysis. (b) Top view of **TSBTQ-6** (1) in space filling packing models with four thio-alkyl chains in clockwise-direction. The red (light red), blue (light blue) and gray (and light gray) colored balls indicate sulphur, nitrogen, and carbon atoms, respectively.



Fig. S5 Output characteristics of solution-sheared OFETs based on TSBTQ-6 film.



Fig. S6 Transfer characteristics of spin-coated OFETs based on TSBTQ-6 film.



Fig. S7 1D diffraction profile with respect to the out-of-plane (OOP) and in-plane (IP) direction of (a) **TSBTQ-6** and (b) **TSBTQ-10** film.



Fig. S8 The operation stability of TSBTQs OFETs.



Fig. S10 ¹³C NMR spectrum of **TSBTQ-6** (1) recorded in CDCl₃.



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Fig. S14 ¹³C NMR spectrum of 4a recorded in CDCl₃.







Fig. S18¹³C NMR spectrum of 5a recorded in CDCl₃.



Fig. S20¹³C NMR spectrum of 5b recorded in CDCl₃.



Fig. S21 (a) Absorption spectra of **TSBTQ** compounds recorded in *o*-dichlorobenzene solution. (b) Solution sheared thin films.



Fig. S22 (a) Cyclic voltammogram of **TSBTQ-10**. (b) Differential pulse voltammogram of **TSBTQ-10**. Both were recorded in the same concentration of *o*-dichlorobenzene solution.