## Electronic supplementary information for

## Electronic properties modulation of tetraoxidothieno[3,2-*b*]thiophene-based

## quinoidal compounds by terminal fluorination

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#### 1. Instruments

 $^{1}\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on Bruker AV 400-MHz spectrometer at 400 and 100 MHz, respectively, in chloroform-d (CDCl<sub>3</sub>) or 1,1,2,2-tetrachloroethane- $d_2$ (C2D2Cl4) at room temperature. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were measured on a Bruker/AutoflexIII Smartbean MALDI spectrometer linear mode with mass in 2-[(2E)-3-(4-tert-buthylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as the matrix. Thermogravimetric analysis (TGA) was conducted under nitrogen on TA Q50 thermogravimetric analyzer at a heating rate of 10 °C/min. UV-vis-NIR absorption spectra were measured by Shimadzu UV3600 spectrometer. The optical bandgap was calculated from the absorption onset of thin-film according to the equation of  $E_g^{opt} = 1240 / \lambda_{onset}$  eV. Cyclic voltammograms (CV) were recorded by a CHI660 electrochemical analyzer with a three-electrode cell at a scan rate of 50 mV/s in anhydrous dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) solution. A glassy carbon with 2 mm diameter, a Pt wire and a saturated calomel electrode (SCE) were used as working electrode electrode. counter and reference electrode. respectively. Tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) with a concentration of 0.1 mol/L was used as supporting electrolyte. The potential was calibrated by ferrocene/ferrocenium (Fc/Fc<sup>+</sup>), which was 0.40 V versus SCE. The lowest unoccupied molecular orbital (LUMO) energy levels were estimated by the equation of LUMO = - (4.80 +  $E_{onset}^{re}$ ) eV, in which  $E_{onset}^{re}$  represents the reduction onset-potentials versus Fc/Fc<sup>+</sup>. X-ray diffraction (XRD) was recorded on Bruker D8

Discover thin-film diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å) operated at 40 kV and 40 mA. Atomic force microscopy (AFM) measurements were tested in tapping mode on a SPA400HV instrument with a SPI 3800 controller (Seiko Instruments). Density functional theory (DFT) optimized molecular geometries, DFT-calculated energy levels, frontier molecular orbital (FMO) distribution, optimal energies of the compounds and rotation energy barriers were conducted by Gaussian 09 with a hybrid B3LYP correlation functional and 6-31G (d) basis set. The branched alkyl side chains were replaced by methyl groups to simplify the calculations. The reorganization energies were carried out from the adiabatic potential surfaces of the natural and negatively charged states. The geometry optimization and frequency analysis of the natural and charged performed states were bv B3LYP(D3BJ)<sup>1-4</sup>/def2-SVP<sup>5</sup> level of theory and single point energies were calculated at the B3LYP(D3BJ)/def2-TZVPD6, 7 level in Gaussian 09 program. The charge transfer integrals for the molecular dimer were calculated at M06-2X<sup>8</sup>/6-311G\*\*9 level in the CT module of NWchem<sup>10</sup> package.

#### 2. Fabrication and characterization of OTFT devices

Bottom-gate/top-contact (BGTC) OFET devices were fabricated on the heavily doped n-type silicon wafers with 300 nm thermally grown SiO<sub>2</sub> (Ci = 10 nF/cm<sup>2</sup>). The substrate was cleaned with acetone, methanol, and deionized water in an ultrasonic bath and then dried under a nitrogen flow, followed by heating at 100 °C for 30 min and a UV-zone treatment for 20 min. Subsequently, the substrates were modified by OTMS. The thin-films were deposited by spin-coating 10 mg/mL chloroform solution in an argon-filled glovebox with 5000 rpm for 30s, followed by heating at 50 °C for 10 min to remove the residual solvent. Finally, gold source and drain electrodes (40 nm) were evaporated on the top of semiconductor layer through a shadow mask with a channel width (W) of 5600  $\mu$ m and a channel length (L) of 50  $\mu$ m. The electrical measurements were performed in an argon-filled glovebox with Keysight B1500A.

Field-effect mobility in saturation regime was calculated by using the equation of  $I_{DS}^{sat} = (\mu C_i W/2L)(V_{GS}-V_T)^2$ , in which  $I_{DS}$  is the drain-source current,  $\mu$  is the field-effect mobility,  $C_i$  is the capacitance per unit area of the dielectric layer,  $V_{GS}$ ,  $V_{DS}$  and  $V_T$  are the gate voltage, drain voltage and threshold voltage, respectively.

## 3. Supplementary Data



Figure S1. The three isomers of compound 4. 4a  $(X_1=X_2=X_3=H)$ , 4b  $(X_1=X_2=H, X_3=F)$ , 4c  $(X_2=H, X_1=X_3=F)$ , 4d  $(X_1=X_2=X_3=F)$ .



Figure S2. The relative energy diagram of the isomers of 4a, 4b, 4c and 4d.



Figure S3. 400 MHz <sup>1</sup>H NMR spectra of IDOTT-S2 solution (in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>) heating at

120 °C for different time.



Figure S4. The relative energy diagram of the isomers of IDOTT, 2FIDOTT,

# **4FIDOTT** and **6FIDOTT**.



Figure S5. The rotation energy barrier for the isomers of compound 4a (a) and

# IDOTT (b).



Figure S6. 400 MHz <sup>1</sup>H NMR spectra of **IDOTT** solution (in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>) heating at 120 °C for different time in air.



Figure S7. TGA curves of IDOTT, 2FIDOTT, 4FIODTT and 6FIDOTT.



Figure S8. DFT-optimized molecular geometries, DFT-calculated energy levels and frontier molecular orbital (FMO) distribution diagrams of IDOTT, 2FIDOTT, 4FIDOTT and 6FIDOTT.





of (a) **2FIDOTT**, (b) **4FIDOTT** and (c) **6FIDOTT**.



Figure S10. The molecular packing diagram of 4FIDOTT in thin-film.



Figure S11. The isomer structures of indophenine.



Figure S12. 400 MHz <sup>1</sup>H NMR spectrum of IDOTT measured in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>.



. Figure S13. 100 MHz <sup>13</sup>C NMR spectrum of IDOTT measured in CDCl<sub>3</sub>.



Figure S14. 400 MHz <sup>1</sup>H NMR spectrum of 2FIDOTT measured in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>.



Figure S15. 100 MHz <sup>13</sup>C NMR spectrum of 2FIDOTT measured in CDCl<sub>3</sub>.



Figure S16. 400 MHz <sup>1</sup>H NMR spectrum of 4FIDOTT measured in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>.



Figure S17. 100 MHz  $^{13}$ C NMR spectrum of 4FIDOTT measured in CDCl<sub>3</sub>.



Figure S18. 400 MHz <sup>1</sup>H NMR spectrum of 6FIDOTT measured in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>.



Figure S19. 100 MHz <sup>13</sup>C NMR spectrum of 6FIDOTT measured in CDCl<sub>3</sub>.

Compound	Annealing temperature (°C)	$\mu_{e}^{max} \ (\mu_{e}^{ave}) \ [cm^2 \ V^{-1} \ s^{-1}]^{b}$	$V_{\mathrm{th}}[\mathrm{V}]^{\mathrm{c}}$	$I_{\rm on}/I_{\rm off}{}^{\rm d}$
IDOTT	50	$0.082~(0.073\pm0.0068)$	10	10 <sup>5</sup>
	80	$0.059~(0.052\pm0.0049)$	14	104
	100	$0.034~(0.028\pm0.0057)$	13	10 <sup>4</sup>
2FIDOTT	50	$0.047~(0.036\pm0.0071)$	15	105
	80	$0.029\;(0.024\pm0.0057)$	19	104
	100	$0.0098~(0.0087\pm0.00077)$	21	104
4FIDOTT	50	$0.16\;(0.12\pm0.031)$	12	10 <sup>5</sup>
	80	$0.079\;(0.074\pm0.0042)$	20	104
	100	$0.054~(0.048\pm0.0054)$	23	104
6FIDOTT	50	$0.011\;(0.0097\pm 0.00078)$	9	105
	80	$0.0064~(0.0053\pm0.00099)$	17	104
	100	$0.0019~(0.0012\pm0.00048)$	17	104

**Table S1.** Performance of the OTFT devices with different annealing temperatures.

## 4. X-ray crystallography

The single crystals of compounds **2FIDOTT**, **4FIDOTT** and **6FIDOTT** were grown by diffusion of isopropanol into their chloroform solutions. The data were collected on a "Bruker APEX-II CCD" diffractometer. In the Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation.

Empirical formula	C <sub>38</sub> H <sub>42</sub> F <sub>2</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub>		
Formula weight	724.85		
Temperature	173(2) K		
Wavelength	1.34138 Å		
Crystal system	Triclinic		
Space group	P1		
Unit cell dimensions	a = 8.932(9) Å	a= 107.92(6)°.	
	b = 10.432(10)  Å	b=101.52(8)°.	
	c = 11.11(2)  Å	$g = 106.59(3)^{\circ}$ .	
Volume	896(2) Å <sup>3</sup>		
Z	1		
Density (calculated)	1.343 Mg/m <sup>3</sup>		
Absorption coefficient	1.205 mm <sup>-1</sup>		
F(000)	382		
Crystal size	0.100 x 0.100 x 0.005 mm <sup>3</sup>		
Theta range for data collection	3.833 to 52.026°.		
Index ranges	-10<=h<=10, -12<=k<=11, -12<=l<=12		
Reflections collected	6627		
Independent reflections	5146 [R(int) = 0.0719]		
Completeness to theta = $52.026^{\circ}$	96.7 %		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Data / restraints / parameters	5146 / 1107 / 439		
Goodness-of-fit on F <sup>2</sup>	1.029		
Final R indices [I>2sigma(I)]	R1 = 0.0658, wR2 = 0.1686		
R indices (all data)	R1 = 0.1172, wR2 = 0.2024		
Absolute structure parameter	0.53(12)		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.475 and -0.308 e.Å <sup>-3</sup>		

 Table S2. Crystal data and structure refinement for compound 2FIDOTT.

Empirical formula	C <sub>38</sub> H <sub>40</sub> F <sub>4</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub>		
Formula weight	760.84		
Temperature	193(2) K		
Wavelength	1.34139 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 9.9206(6) Å	a= 96.885(4)°.	
	b = 11.9585(7) Å	b=	
103.220(4)°.			
	c = 15.9638(10)  Å	$g = 92.562(3)^{\circ}$ .	
Volume	1825.29(19) Å <sup>3</sup>		
Z	2		
Density (calculated)	1.384 Mg/m <sup>3</sup>		
Absorption coefficient	1.253 mm <sup>-1</sup>		
F(000)	796		
Crystal size	0.170 x 0.130 x 0.110 mm <sup>3</sup>		
Theta range for data collection	3.823 to 52.990°.		
Index ranges	-10<=h<=11, -14<=k<=14, -18<=l<=18		
Reflections collected	21142		
Independent reflections	6429 [R(int) = 0.0903]		
Completeness to theta = $52.990^{\circ}$	99.7 %		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Data / restraints / parameters	6429 / 225 / 467		
Goodness-of-fit on F <sup>2</sup>	1.063		
Final R indices [I>2sigma(I)]	R1 = 0.0805, WR2 = 0.1595		
R indices (all data)	R1 = 0.1526, wR2 = 0.1859		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.700 and -0.532 e.Å <sup>-3</sup>		

 Table S3. Crystal data and structure refinement for compound 4FIDOTT.

Empirical formula	C <sub>38</sub> H <sub>38</sub> F <sub>6</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub>		
Formula weight	796.82		
Temperature	193(2) K		
Wavelength	1.34139 Å		
Crystal system	Monoclinic		
Space group	C2/c		
Unit cell dimensions	a = 31.086(3) Å	a= 90°.	
	b = 5.1224(4) Å	b=	
115.685(4)°.			
	c = 24.4139(19) Å	$g = 90^{\circ}$ .	
Volume	3503.4(5) Å <sup>3</sup>		
Ζ	4		
Density (calculated)	1.511 Mg/m <sup>3</sup>		
Absorption coefficient	1.378 mm <sup>-1</sup>		
F(000)	1656		
Crystal size	0.180 x 0.160 x 0.040 mm <sup>3</sup>		
Theta range for data collection	2.744 to 52.999°.		
Index ranges	-36<=h<=36, -4<=k<=6, -22<=1<=29		
Reflections collected	11708		
Independent reflections	3072 [R(int) = 0.0643]		
Completeness to theta = $52.999^{\circ}$	99.5 %		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Data / restraints / parameters	3072 / 6 / 250		
Goodness-of-fit on F <sup>2</sup>	1.093		
Final R indices [I>2sigma(I)]	R1 = 0.0607, wR2 = 0.1676		
R indices (all data)	R1 = 0.0851, $wR2 = 0.1886$		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.425 and -0.515 e.Å <sup>-3</sup>		

 Table S4. Crystal data and structure refinement for compound 6FIDOTT.

#### 5. References

- 1. C. Lee, W. Yang and R. G. Parr, *Physical Review B*, 1988, **37**, 785-789.
- 2. B. Miehlich, A. Savin, H. Stoll and H. Preuss, Chem. Phys. Lett., 1989, 157, 200-206.
- 3. A. D. Becke, The Journal of Chemical Physics, 1993, 98, 5648-5652.
- 4. S. Grimme, S. Ehrlich and L. Goerigk, J. Comput. Chem., 2011, 32, 1456-1465.
- 5. A. Schäfer, H. Horn and R. Ahlrichs, *The Journal of Chemical Physics*, 1992, **97**, 2571-2577.
- 6. F. Weigend and R. Ahlrichs, *PCCP*, 2005, 7, 3297-3305.
- 7. D. Rappoport and F. Furche, *The Journal of Chemical Physics*, 2010, **133**, 134105.
- 8. Y. Zhao and D. G. Truhlar, Theor. Chem. Acc., 2008, 120, 215-241.
- 9. P. C. Hariharan and J. A. Pople, *Theoretica chimica acta*, 1973, 28, 213-222.
- M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, T. P. Straatsma, H. J. J. Van Dam, D. Wang, J. Nieplocha, E. Apra, T. L. Windus and W. A. de Jong, *Comput. Phys. Commun.*, 2010, **181**, 1477-1489.