# Electronic Supplementary Information

# $\pi$ -core tailoring for new high performance thieno(bis)imide based

# n-type molecular semiconductors

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#### 1. Synthesis

**General**. Compounds **NBr** and **NT4N**, **3** were prepared according to already reported procedures.<sup>1</sup> 2,5bis(trimethylstannyl)thieno[3,2-b]thiophene is a commercially available compound. The synthesis of 5,5'bis(tributylstannyl)-2,2'-bithiazole stannylated cores (ThT, Tz ) was performed under already reported metallation conditions.<sup>2</sup> The synthesis of (3,3'-dimethyl-[2,2'-bithiophene]-5,5'-diyl)bis(tributylstannane) core (TMe) is described below. All <sup>1</sup>H, and <sup>13</sup>C NMR spectra were recorded with a Varian Mercury 400 spectrometer operating at 400 MHz (<sup>1</sup>H). Chemical shifts were calibrated using the internal CDCl<sub>3</sub>, resonance which were referenced to TMS. Mass spectra were collected on a ion trap Finningan Mat GCQ spectrometer operating in electron impact (EI) ionization mode. Each sample was introduced to the ion source region of GCQ via a direct exposure probe (DEP). Melting points (uncorrected) were determined on a 'hot-stage' apparatus where the melting process was observed with the aid of a microscope.

General Stille coupling procedure for the synthesis of compounds 1-3. To a refluxing toluene solution of in situ prepared Pd(AsPh<sub>3</sub>)<sub>4</sub> (8 mol%) under N<sub>2</sub> atmosphere, and compound N-Br the appropriate tributylstannyl derivative diluted in toluene was added dropwise. The solution is refluxed for 8 h, then the solvent is removed under vacuum, and the crude purified by chromatography on silica gel (pentane/CH<sub>2</sub>Cl<sub>2</sub> =  $50/50 \rightarrow CH_2Cl_2$  100% as the eluent) followed by crystallization from toluene.

**2,2'-([2,2'-bithiazole]-5,5'-diyl)bis(5-butyl-4H-thieno[2,3-c]pyrrole-4,6(5H)-dione), NTzN, 1:** 44% Yield. M.p. > 375°, MS (70 eV, EI): m/z 582 (M<sup>+1</sup>),  $\lambda_{max}$ , CH<sub>2</sub>Cl<sub>2</sub> = 427nm,  $\lambda_{em}$ , CH<sub>2</sub>Cl<sub>2</sub> = 514nm, 488 nm. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS/ppm): 8.08 (s, 2 H), 7.44 (s, 2 H), 3.63 (t, 4H), 1.64 (m, 4H), 1.36 (m, 4H), 0.95 (t, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS/ppm): 163.5, 162.3, 160.8, 145.2, 144.7, 141.7, 139.6, 133.2, 119.2, 38.5, 30.8, 20.0, 13.6. Anal. calcd for C<sub>26</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub>S<sub>4</sub>: C, 53.59; H, 3.81; N, 9.61 Found C, 53.68; H, 3.89; N, 9.58.

**2,2'-(thieno[3,2-b]thiophene-2,5-diyl)bis(5-butyl-4H-thieno[2,3-c]pyrrole-4,6(5H)-dione), NThTN, 2:** 54% Yield. M.p. >365°, MS (70 eV, EI): m/z 554 (M<sup>·+1</sup>),  $\lambda_{max}$ , CH<sub>2</sub>Cl<sub>2</sub> = 441 nm ,  $\lambda_{em}$ , CH<sub>2</sub>Cl<sub>2 = 545 nm, <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS/ppm)  $\delta$ : 7.49 (s, 2 H), 7.38 (s, 2 H), 3.62 (t, 4H), 1.64 (m, 4H), 1.37 (m, 4H), 0.95 (t, 6H). Anal. calcd for C<sub>26</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>S<sub>4</sub> C, 56.29; H, 4.00; N, 5.05 Found C, 56.37; H, 4.07; N, 5.07.</sub>

#### 2,2'-(4,4'-dimethyl-[2,2'-bithiophene]-5,5'-diyl)bis(5-butyl-4H-thieno[2,3-c]pyrrole-4,6(5H)-dione)

**NTMEN, 3:** 64% Yield, M.p. = 248°, MS (70 eV, EI): m/z 608 (M<sup>·+1</sup>),  $\lambda_{max}$ , CH<sub>2</sub>Cl<sub>2</sub> = 449 nm,  $\lambda_{em}$ , CH<sub>2</sub>Cl<sub>2</sub> = 580 nm. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS/ppm): 7.30 (s, 2 H), 7.04 (s, 2 H), 3.62 (t, 4H), 2.43 (s, 6H), 1.64 (m, 4H), 1.36 (m, 4H), 0.95 (t, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS/ppm): 164.1, 162.8, 148.9, 144.9 138.1, 137.6, 135.9, 128.9, 118.2, 38.3, 30.9, 20.0, 15.9, 13.6. Anal. calcd for C<sub>30</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>S<sub>4</sub>: C, 59.18; H, 4.64; N, 4.60, Found: C, 59.25; H, 4.70; N, 4.62;

(3,3'-dimethyl-[2,2'-bithiophene]-5,5'-diyl)bis(tributylstannane): To anhydrous solution of the dibromo precursor (0,192 g ; 0,54 mmol) in 6 ml of Et<sub>2</sub>O under nitrogen, BuLi (2,5 M in hexane) was added dropwise (0,48 ml, 1,19 mmol) at -50° and the solution stirred for 2 h. Then Bu<sub>3</sub>SnCl (0,360 g ; 1,1 mmol) was added dropwise and the solution stirred overnight. The reaction was quenched by adding 10 ml of water. Conventional workup and evaporation of the solvent afforded the target compound as brown oil (0,400 g; yeld 96 %). MS (70 eV, EI): m/z 770 (M<sup>·+1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS/ppm): 7.08 (s, 2 H), 2.26 (s, 6H), 1.56 (m, 12H), 1.34 (m, 12H), 1.13 (t, 12H), 0.92 (t, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS/ppm): 145.6, 142.7, 130.8, 127.1, 29.0, 27.3, 17.9, 13.6, 10.8.

1. M. Melucci, M. Zambianchi, L. Favaretto, M. Gazzano, A. Zanelli, M. Monari, R. Capelli, S. Troisi, S. Toffanin, M. Muccini, *Chem. Commun.*, 2011, **47**, 11840.

# 2. <sup>1</sup>H-NMR spectra



**Fig. SI\_1.** <sup>1</sup>HNMR spectrum of NTzN (400 MHz, CHCl<sub>3</sub>).



**Fig. SI\_2.** <sup>1</sup>HNMR spectrum of NThTN (400 MHz, CHCl<sub>3</sub>).



Fig. SI\_3. <sup>1</sup>HNMR spectrum of NTMeN (400 MHz, CHCl<sub>3</sub>).

# 3. Thermal analysis

Differential Scanning Calorimetry (DSC) analysis was performed by using a Thass DSC-XP-10 instrument under atmospheric conditions.



Fig. S\_4. a) DSC thermogram of compound NTzN, 1.



Fig. S\_5. a) DSC thermogram of NThTN, 2.



Fig. S\_6. DSC thermogram of NTMeN, 3.

# 4. Cyclic Voltammetry (CVs)

Cyclic voltammetries have been carried out at room temperature, after Ar purging, with an AMEL 5000 Electrochemical System in  $CH_2Cl_2$  (Carlo Erba RPE, distilled over anhidrous  $P_2O_5$  and stored under Ar pressure) and 0.1 M ( $C_4H_9$ )<sub>4</sub>NClO<sub>4</sub> (Fluka, puriss. crystallized from methanol and vacuum dried) saturated with the compounds under study (concentration less than 1 mM). The electrochemical cell was in three compartment shape, with Pt spherical electrode (diameter 2 mm), Pt wire counter electrode and aqueous KCl Saturated Calomel Electrode. The standard potential of ferrocene/ferricinium in  $CH_2Cl_2$  0.1 M ( $C_4H_9$ )<sub>4</sub>NClO<sub>4</sub> resulted 0.47 V vs. SCE, consequently the absolute energy of SCE in  $CH_2Cl_2$  0.1 M ( $C_4H_9$ )<sub>4</sub>NClO<sub>4</sub> has been estimated as -4.37 eV.

### 5. Theoretical calculations

The geometry of all compounds was optimized in their ground state in vacuum using the B3LYP<sup>1</sup> exchange-correlation functional and 6-31G\* basis set,<sup>2</sup> using the Gaussian03 <sup>3</sup> program package. Single point calculations were performed in CH<sub>3</sub>CN solution, using the C-PCM <sup>4</sup> solvation model.

<sup>1.</sup> A. D. Becke, J. Chem. Phys. 1993, 98, 5648.

<sup>2.</sup> R. Ditchfield, W. J. Hehre, J. A. Pople, J. Chem. Phys. 1971, 54, 724.

Frisch, M. J., G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J.

W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople., Gaussian 03, Revision C.02. Gaussian, Inc., Wallingford, CT, . In 2004.

4. a) S. Miertuš, E. S. J. Tomasi Chem. Phys. 1981, 55, 117; b) M. Cossi, V. Barone, J. Chem. Phys. 2001, 115, 4708.

#### 6. Thin deposits and lithographically controlled wetting (LCW)

*Materials.* Sylgard 184 (polydimethylsiloxane) silicone elastomer base and curing agent were purchased from Dow Corning. Chloroform (anhydrous,  $\geq$ 99.8%) and dichloromethane were purchased from Aldrich (anhydrous,  $\geq$ 99.9%). Optical micrographs were recorded with a Nikon i-80 microscope equipped with epi-illuminator, and cross polars.

Substrate cleaning and preparation. Silicon wafers with a thermally grown silicon dioxide layer (200 nm thick) or glass slides are used as substrates ( $10 \times 10 \text{ mm}^2$ ). All substrates were cleaned by sonication in acetone for 10 min, then in 2-propanol for 10 min, and dry in a stream of nitrogen prior to use.

**Stamp preparation.** The elastomeric polydimethylsiloxane (PDMS) stamps were prepared by replica molding<sup>1</sup> of a blank Compact Disk (periodicity of 1.6  $\mu$ m, FWHM = 1  $\mu$ m and 220 nm deep). After curing for 6 h at 60°C, PDMS stamps were peeled off, cleaned by sonication in ethanol for 10 min, and dry in N<sub>2</sub>.

**Sample preparation.** LCW method was performed according to the detailed protocol.<sup>2</sup> In brief, 5  $\mu$ L of 1 mg/mL chloroform solution of each compoundpreviously filtered through a 0.2  $\mu$ m RC filter, are drop cast on the substrate, and then a PDMS stamp (5 × 5 mm<sup>2</sup>) is placed on the top. After the complete evaporation of the solvent (24 h), the stamp is gently removed and, before characterization, the sample is aged in atmospheric conditions for 2 hours. Drop cast films were prepared without using elastomeric stamps.

2. M. Cavallini, D. Gentili, P. Greco, F. Valle and F. Biscarini, *Nat. Protocols*, 2012, 7, 1668-1676.

<sup>1.</sup> Y. N. Xia and G. M. Whitesides, Angew. Chem.-Int. Edit., 1998, 37, 551-575.



**Fig. S\_7.** Optical micrographs of  $\mu$ -stripes recorded: a) under un-polarized light, b) with crossed polars oriented along the axes of the image, c) with crossed polars oriented along the axes of the image rotating the sample ~30°.

Although some cracks appear in the stripes,  $\mu$ -stripes appear very homogeneous (Fig. S 7a-c) and exhibit the typical behaviour of optically anisotropic materials exhibiting birefringence. In particular, the  $\mu$ -stripes appear homogeneously colored, this indicates that their thickness is almost constant over the entire stripe. The  $\mu$ -stripes extinguish in four positions at intervals of 90°. Albeit the presence of the craks, the occurrence of light extinction at the same orientations in the all places of a single  $\mu$ -stripe (Fig. S7 b) suggests that the crystalline domains are grown with the same orientation inside each stripe. However, the variation of the angle of extinguishment for different stripes (Fig. S7 c) indicates that each stripes has a different crystallographic orientation. By this behaviour, we deduced that the confined deposition by LCW has induced a coherent, long-range order along the direction of the stripes independently for each stripe.

## 7. Device fabrication

The transistors were fabricated in bottom gate-top contact geometry. The ITO substrate cleaning procedure consists of two sonication cycles, first in acetone and then in 2-isopropanol, for 10

minutes each. The 450 nm thick dielectric layer of PMMA has been grown by spin-coating on top of the clean ITO substrate (relative electric permittivity  $\varepsilon = 3.6$  at 100 Hz). The PMMA film was then thermally annealed in a glove box at 120°C (around 10°C above the glass transition temperature for PMMA) for 15 hours under inert atmosphere. (CPMMA = 7.08 nF/cm2).

The 30 nm thick layers have been grown by vacuum sublimation in a home-made vacuum chamber, with a deposition rate of 0.1 Å/s, at a base pressure of 10 -6 mbar. The substrate temperature during the film deposition has been kept at room temperature (RT). The drain-source electrodes were made of gold and were evaporated through a shadow mask on top of the organic thin film. The gold layer thickness is 50 nm, while the channel length and the channel width are 70  $\mu$ m and 15 mm, respectively.

The electronic measurements have been carried out in a controlled nitrogen atmosphere (dry box,  $O_2$  and  $H_2O < 1ppm$ ) using a commercial Suss PM5 probe station interfaced with an Agilent B1500A parameter analyser.



Fig. S\_8. Saturation transfer and linear transfer curves for NTzN.



# Locus curve P type

Saturation Transfer curve N type



Fig. S\_9. Locus and transfer curves for NThTN.



-40

 $V_{gs} = V_{Ds} (V)$ 

-60

-80

-100

Ó

-20







Saturation Transfer curve N type



Saturation Transfer curve P type



Fig. S\_10. Locus and transfer curves for NTMeTN.

## 8. Electrical Parameters Extraction and data elaboration



The mobility and the threshold voltage of the OFETs are extracted by the locus curve by performing a linear fit of the square root (SQRT) of the curve tail. The mobilities, were calculated by the angular coefficient of the linear part of locus SQRT, while the device threshold voltages were extracted by the intercept of the linear part of SQRT of the locus.