The synthesis and characterization of two thieno(bis)imidazole based n-type semiconductors with electron mobilities of up to 0.3 cm² V⁻¹ s⁻¹ are described. The relationships between the electronic features of the n-inner core and the functional properties of the new materials are also discussed.

Organic field effect transistors (OFETs) based on \( \pi \)-conjugated molecular materials attract great attention because of many advantages in contrast to conventional silicon-based transistors, for instance, low fabrication cost, large-area manufacturing, and flexibility. Among molecular materials, thiophene-based ones are widely investigated for their chemical versatility and functionality as p-type semiconductors. In contrast, thiophene based molecular materials featuring electron and ambipolar charge transport have been more rarely documented.

Arylene(bis)imide frameworks are commonly exploited building blocks to promote electron and ambipolar charge transport. A combination of phenylene(bis)imidazole frameworks (n-type blocks) and oligothiophenes (p-type blocks) has been proposed as a two block strategy toward the synthesis of ambipolar semiconductors. In this segment, we have recently developed the thiophene(bis)imidazole (TBI, N) moiety as an end group capable of promoting ambipolar charge transport in quaterthiophene. Indeed, T4DIM having two TBI end moieties of bithiophene (TT) showed ambipolar charge transport with major electron charge transport contribution and mobilities of up to \( \mu_e = 5.3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \). In accordance with the current need for highly performing electron charge transport materials, we report here two novel compounds featuring fine-tunable inner cores such as: bithiazole (Tz \to NTzN, Scheme 1) and thiophenothiazine (TTz \to NThTN, Scheme 1). Thiophenothiazine insertion into linear oligothiophenes has been related to efficient hole charge transport. In contrast, the insertion of thiazole rings into trifluorophenyl ended oligothiophenes improves electron charge transport and threshold voltages with respect to all-thiophene based analogues. Accordingly, we envisioned the possibility of controlling the n-type behaviour of TBI based semiconductors by using \( \pi \)-inner cores more electron-deficient than TT (as for T4DIM). To further validate this strategy, a probe compound featuring a dimethylated bithiophene inner core was also synthesized and investigated (TMe \to NTMeN, Scheme 1).

The title compounds were prepared through Stille cross-coupling reaction between brominated thieno(bis)imidazole (N-Br) and the proper distannyl derivative as depicted in Scheme 1. Differential scanning calorimetry (DSC, Fig. S1–S3, ESI‡) revealed liquid crystalline properties of NThTN and NTMeN.

The UV-Vis absorption and emission spectra of compounds 1–3 are shown in Fig. 1a and the complete list of the optical and electrochemical data is summarized in Table 1. Interestingly, the introduction of the Tz core causes a blue shift of the maximum

Scheme 1: Synthetic route to compounds 1–3. (i) 5 mol% of in situ formed Pd(AsPh₃)₄, refluxing toluene.
absorption wavelength $\lambda_{\text{max}}$ of about 15 nm and 20 nm with respect to NThTN and NTMeN respectively. The same trend is observed for the maximum emission wavelengths that are strongly blue shifted for NTzN with respect to the other compounds.

In detail, NTzN showed structured emission with two maxima located at 489 nm and 514 nm respectively. NThTN and NTMeN displayed unstructured emission with the maxima shifted by 32 nm and 67 nm respectively (Fig. 1a). The optical energy band gap $E_{\text{opt}}^g$ of NTzN was about 0.10 eV higher than those of the other compounds.$^{11a}$

CVs of compounds NTzN and NThTN show a quasi-reversible reduction wave$^{12}$ while NTMeN shows both reduction and oxidation quasi-reversible waves in the electrochemical window of the electrolytic solution (Fig. 1b), in agreement with the smaller $E_{\text{opt}}^g$ (Table 1). The reduction potential $E_{\text{red}}$ becomes more negative on passing from NTzN to NTMeN suggesting a less delocalized LUMO in the latter.

Accordingly, DFT calculations performed with the B3LYP functional$^{13}$ and a 6-31G* basis set show that in NTzN both the HOMO and LUMO are almost uniformly delocalized on the entire molecular backbone (Fig. 1c). In contrast, for NThTN and NTMeN the HOMO is mainly localized in the inner core while the LUMO is localized at the periphery of the electron-withdrawing TBI ends.

Such orbital distribution suggests higher suitability to charge transport for NTzN since higher intermolecular overlap (favourable to charge transport) can be expected for conjugated oligomers having uniformly distributed frontier orbitals.$^{16,14}$

Thin deposits of the newly synthesized compounds were analysed by polarised optical microscopy (POM) to investigate the self-organization capability of these materials at the surface. Upon drop casting, all compounds form isolated micrometre sized, birefringent crystals whose shape depends on the substrate and the solvent used.

(Fig. 2b).$^{15a}$ However, lithographically controlled wetting (LCW, Fig. 2a)$^{15b,c}$ allows the fabrication of parallel micrometre-sized stripes ($\mu$-stripes) of a few millimetres length (Fig. 2c) covering the entire substrate. Despite some cracks that are present along some $\mu$-stripes, detailed investigation by POM (see ESI$^+$) reveals long range coherent molecular ordering along each stripe. The electrical properties of the

### Table 1 List of experimental and calculated optoelectronic parameters

<table>
<thead>
<tr>
<th>Comp.</th>
<th>$\lambda_{\text{abs}}$ a (nm)</th>
<th>$\lambda_{\text{em}}$ a (nm)</th>
<th>$E_{\text{opt}}^g$ b (V)</th>
<th>$E_{\text{opt}}^b$ b (V)</th>
<th>$E_{\text{HOMO}}$ (eV) (theor)</th>
<th>$E_{\text{LUMO}}$ c (eV) (theor)</th>
<th>$E_{\text{opt}}^d$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTzN</td>
<td>428</td>
<td>489/514</td>
<td>&gt;1.6</td>
<td>-1.13</td>
<td>-5.81$^d$ (-5.89)</td>
<td>-3.24 (-3.00)</td>
<td>2.57</td>
</tr>
<tr>
<td>NThTN</td>
<td>443</td>
<td>546</td>
<td>&gt;1.6</td>
<td>-1.2</td>
<td>-5.69$^d$ (-5.58)</td>
<td>-3.2 (-2.79)</td>
<td>2.49</td>
</tr>
<tr>
<td>NTMeN</td>
<td>449</td>
<td>581</td>
<td>&gt;1.28</td>
<td>-1.26</td>
<td>-5.65$^d$ (-5.38)</td>
<td>-3.11 (-2.73)</td>
<td>2.39</td>
</tr>
</tbody>
</table>

a In CH$_2$Cl$_2$. b Vs. SCE in CH$_2$Cl$_2$ containing 0.1 mol L$^{-1}$ (C$_4$H$_9$)$_4$NClO$_4$. c $E_{\text{LUMO}} = e(4.37 + E_{\text{opt}}^b)$. 

d $E_{\text{opt}}^d = 1240/\lambda_{\text{opt}}$. 

e $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{opt}}^d$. 

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newly synthesized materials were measured in bottom gate-top contact OFET devices (nitrogen atmosphere, 1 ppm O₂, 1 ppm H₂O, other details in ESI†). The device responses are reported in Fig. 3 showing the multiple output curves for each compound. NTzN shows exclusively electron charge transport with charge mobility values of up to $\mu_e = 0.16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a threshold voltage $V_{\text{TH}} = -3.7 \text{ V}$ (Table 2). In contrast, NTiTN shows ambipolar charge transport with an excellent electron charge mobility of $\mu_e = 0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ but a higher threshold voltage (with respect to NTzN) and a hole mobility of $\mu_h = 6.4 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Table 2). Both mobility values are orders of magnitude higher than that observed for the already reported T4DIM9 ($\mu_e = 5.3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and comparable or even better than the best performances so far achieved for n-type thiophene based materials.16 It should be noted that no device optimization (i.e. substrate functionalization or annealing procedures) was performed. The electron mobilities drop by about three orders of magnitude on passing to NTMeN having the more electron rich methylated thiophene inner core (Table 2).

Although the beta methyl substitution could prevent a close molecular overlap required for efficient charge transport, it appears that electron deficient cores strongly improve the charge transport capability of thiено(bis)imide based materials. The unipolar rather than ambipolar behaviour observed for NTzN could be due to the less favourable matching of the estimated HOMO energy of NTzN (lower than the other compounds) with the gold electrode FERMI level which limits the hole injection. In conclusion, two new efficient and highly processable n-type molecular semiconductors based on the combination of thiено(bis)imide end units with thiazole and thienothiophene π-inner cores have been presented. Electron charge mobility values of up to 0.3 $\text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (in un-optimized devices) were measured for these materials.

Such OFET performance is one order of magnitude higher than those achieved by using unsubstituted thiophene π-cores (T4DIM) and three orders of magnitude higher with respect to NTMeN having a more electron rich core. Given the lack of n-type materials and the poor level of understanding of their structure–property relationships, these results provide important perspectives towards the development of new molecular n-type semiconductors.

Current work is focused on the use of different cores as well as on the device tailoring to further improve the electrical performance. The authors gratefully acknowledge the support of this work by the Consorzio MIST-ER through project FESR-technopol AMBI-MAT, by the EU through project FP7-ICT-248052 (PHOTO-FET) and by the Italian MISE through project Industria 2015 (ALADIN). MC and DG were supported by the Project European Science Foundation EURYI DYMO. MM thanks L. Favaretto and M. Zambianchi for their precious support.