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# Molecular tuning in highly fluorescent dithieno[3,2-*b*:2',3'-*d*]pyrrole-based oligomers: effects of N-functionalization and terminal aryl unit<sup>†</sup>

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A series of eight conjugated oligomers consisting of central dithieno[3,2-*b*:2',3'-*d*]pyrroles (DTPs) end-capped with either thienyl or phenyl groups have been prepared from *N*-alkyl-, *N*-aryl-, and *N*-acyl-dithieno[3,2-*b*:2',3'-*d*]pyrroles *via* Stille and Suzuki cross-coupling. The DTP-based quaterthiophene, *N*-phenyl-2,6-bis(2-thienyl)dithieno-[3,2-*b*:2',3'-*d*]pyrrole was characterized *via* X-ray crystallography and was found to crystallize in the orthorhombic space group Pna2<sub>1</sub> with a = 10.8666(3) Å, b = 22.8858(6) Å, c = 7.4246(2) Å, and Z = 4. The full oligomeric series was thoroughly investigated *via* photophysical, electrochemical, and DFT calculations in order to correlate the cumulative effects of both aryl end-groups and N-functionalization on the resulting optical and electronic properties. Through such molecular tuning, it was found to be possible to modulate the HOMO energy by as much as 0.32 V and to generate highly fluorescent oligomers with solution fluorescence efficiencies as high as 92%.

# Introduction

Conjugated organic materials continue to be a topic of considerable fundamental and technological interest as they combine the electronic and optical properties of inorganic semiconductors with a number of distinct advantages typical of organic plastics. Such benefits include light-weight and mechanically-flexible materials, low production costs, and the ability to tune key material properties at a molecular level *via* synthetic modification.<sup>1-4</sup> Within the larger class of conjugated materials, oligomers have played an important role as models of polymeric materials, allowing greater insight into their respective electronic and optical properties. Such oligomeric models allow for strong correlation between observed properties and overall chemical structure, which can be more rigidly controlled in oligomers, particularly in terms of a defined conjugation length.<sup>4-17</sup> Low molecular weight oligomeric materials are also

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typically more soluble than their polymeric analogues and often can be vaporized at reduced pressure. As such, oligomer thin films can be deposited through a variety of methods including solution casting and vacuum sublimation.<sup>7</sup> This ease of processing can make such oligomeric materials useful not only as model compounds, but also as potential active materials for a number of device applications.

Oligothiophenes are thought to be one of the more dynamic classes of conjugated organic oligomers because of their environmental stability, as well as the ease in which they can be synthetically modified.<sup>5</sup> Thiophene chemistry is well established and modification of the core backbone is nearly limitless, allowing extensive tuning of the electronic properties. In addition, the planar structure and strong  $\pi$  interactions of oligothiophenes enhance favourable stacking on substrates and in the bulk, while the polarizability of sulfur leads to excellent charge transport properties.<sup>5</sup> One approach to the synthetic modification of oligothiophenes has been the introduction of fused aromatic units into the conjugated backbone, resulting in materials exhibiting enhanced carrier mobilities and lowered band gaps. Such fused-ring thiophene building blocks include 4H-cyclopenta-[2,1-b:3,4-b']bithiophene (1, CPBT), dithieno[3,2-b:2',3'-d]thiophene (2, DTT), and N-alkyl- or N-aryl-dithieno[3,2-b:2',3'-d]pyrroles (3, DTPs) as shown in Fig. 1. $^{18-25}$ 

In particular, DTPs have found recent popularity and their application to oligomeric systems has resulted in increased conjugation, reasonable hole mobilities, and significantly enhanced solution and solid-state fluorescence properties.<sup>20–25</sup> For example, the fluorescence quantum yield of DTP-based quaterthiophenes have been reported to be as high as 66%, constituting one of

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de Teatinos s/n, Málaga 29071, Spain. E-mail: carmenrd@uma.es † Electronic supplementary information (ESI) available: NMR spectra for all compounds, X-ray data for **3b**, **7b**, and **15a**, and full computational details and results. CCDC reference numbers 863469–863471. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cp40161d



Fig. 1 Fused-ring bithienyl building blocks.

the highest reported for any oligothiophene.<sup>21</sup> In addition, such DTP-based oligomers exhibit measurable solid-state emission and thus such oligomers could be promising materials for organic light emitting diode (OLED) applications.<sup>21</sup>

More recently, successful OLED devices utilizing DTP-based polymeric materials have been reported in which it was found that the solution and solid-state emission of the DTP-based materials were significantly enhanced *via* copolymerization with arylene units.<sup>26</sup> In order to model such DTP-arylene materials and to strengthen our understanding of the structure-property relationships of DTP-based oligomers, a series of 2,6-bis(2-thienyl)- and 2,6-bis(phenyl)-substituted DTPs (**7**,**8** and **12**,**13** respectively, as shown in Fig. 2) have been prepared in order to thoroughly investigate the effect of the aryl endgroups on the oligomer properties.

Despite the popularity and success of DTP-based materials, the high energy of the DTP HOMO has been viewed as a limitation which can hinder stability and the effective application of DTP-based materials to various devices. As a solution, a new class of DTPs incorporating N-acyl groups have been recently reported.<sup>19</sup> The resulting *N*-acylDTPs exhibit stabilized HOMO and LUMO energy levels, as well as a slight red-shift in absorption energies. To further investigate the effect of these 'second generation' DTP building blocks, oligomers **8** and **13** have been included in the current study in order to fully investigate the molecular tuning effects of both aryl endgroups (*i.e.* **7** *vs.* **12**; **8** *vs.* **13**) and N-functionalities (*i.e.* **7** *vs.* **13**).



Fig. 2 Quaterthiophenes and phenyl-capped analogues.

# Synthesis

As previously reported, both first and second generation N-functionalized dithieno[3,2-*b*:2',3'-*d*]pyrroles (**3**) can be readily synthesized from 3,3'-dibromo-2,2'-bithiophene.<sup>19,26</sup> N-Functionalized DTPs can then be incorporated into oligomer backbones *via* either Stille or Suzuki coupling methods as shown in Scheme 1. The distannyl intermediates (**14**) of either *N*-alkyl- or *N*-arylDTPs were generated from a previously reported procedure in nearly quantitative yields.<sup>26</sup> Reaction with the appropriate arylbromide *via* Stille cross-coupling<sup>27</sup> allowed production of oligomers **7** and **12** in moderate to good yield (41–81%).

In the application of the *N*-acylDTPs, a different approach is required due to the susceptibility of the acyl carbonyl to nucleophilic attack, which eliminates the use of processes requiring deprotonation *via* BuLi. However, *N*-acylDTPs can be readily brominated *via* treatment with NBS giving the dibromo intermediates (**15**) as stable species in high yield (70–95%). This is in marked contrast to the *N*-alkylDTPs for which the dibromides are extremely reactive and are prone to readily decompose *via* polymerization.<sup>28</sup> Intermediates **15** can then be used to produce the corresponding *N*-acylDTP-based oligomers **8** or **13** *via* either Stille or Suzuki<sup>29</sup> cross-coupling in moderate yields (32–47%).

### X-ray crystallography

There has been relatively little structural data reported for oligothiophenes, particularly for species containing fused-ring units such as DTT or DTP. While structures of a few DTT-based oligomers have been reported,<sup>30-32</sup> DTP-based structures have been limited primarily to the DTP monomers.<sup>18,19</sup> Only three structures



Scheme 1 Synthesis of DTP-based oligomers.



**Fig. 3** Face (A) and edge (B) ellipsoid plots of oligomer **7b** at the 50% probability level.

of larger oligomeric species have been previously reported, those of quaterthiophene 7c,<sup>21</sup> a tetra(2,5-dimethylthien-3-yl)capped DTP<sup>25</sup> and a bis[(diphenylamino)phenylene]-capped DTP.<sup>22b</sup> Recently, however, oligomer 7b has been successfully crystallized and its determined structure is shown in Fig. 3. Selected bond distances and angles for 7b are given in Table 1, along with those for 3b and 7c for comparison.

Oligomer 7b crystallizes in the orthorhombic space group Pna2<sub>1</sub>, with four molecules per unit cell. The central DTP unit is fairly planar with a slight sigmoidal distortion (mean deviation of 0.059 Å) and its bond lengths and angles are in good agreement with the analogous DTP monomer 3b. Both external thiophene rings are rotated out of the plane of the central DTP unit, with torsion angles of  $23.8^{\circ}$  and  $21.0^{\circ}$ , respectively. This is consistent with the structure of 7c and agrees well with current (see supporting information) and previous<sup>21</sup> DFT geometry optimizations exhibiting torsion angles of  $\sim 20^{\circ}$  between the terminal thiophenes and the DTP unit. In a similar manner, the N-phenyl group is also out of the plane of the DTP unit, with a torsion angle of 46.1°. While this is greater than the analogous torsion angle of 37.0° observed in DTP 3b, it does fall within the range of angles exhibited by all known N-phenylDTP structures  $(37.0-49.7^{\circ})^{18,22b,33}$  and is in excellent agreement with the value predicted by its DFT-optimized structure (44.1°).

Typical of all DTPs, the fused bond between the heterocycles (*i.e.* C(5)–C(11) = 1.396 Å, C(4)–C(19) = 1.391 Å) is elongated compared to thiophene (1.370 Å) and is more consistent with pyrrole (1.382 Å).<sup>34</sup> Due to the presence of the pyrrole ring, the C(4)–C(5) distance (1.415 Å) of **7b** is slightly shorter than the corresponding central interannular bond of quaterthiophene (**4**), although it is fairly consistent with the analogous bond of pyrrole. The corresponding interannular bond lengths (1.46 and 1.45 Å) between the central DTP and the terminal thiophenes, however, are in good agreement with the interannular bonds of **4** (1.45 Å).<sup>35</sup>

The external thiophenes exhibit some deviations from typical thiophene geometry due to positional disorder resulting from a portion of these rings that are rotated 180° around the interannular bond, resulting in some mixing of the S3/C8 (*ca.* 9.64%) and S4/C12 (*ca.* 12.98%) positions. Such disorder has been previously observed for dialkylsexithiophenes,<sup>36</sup> as well as for **7c.**<sup>21</sup> Other deviations include shortened external  $\alpha,\beta$ -C–C

 Table 1
 Selected Experimental Geometric Parameters of DTP-based

 Quaterthiophenes 7b and 7c, and DTP 3b

Parameter	7b	$\mathbf{7c}^{a}$	3b
S(3)-C(7)	1.703(3)	1.643(2)	_
S(3) - C(22)	1.699(3)	1.583(3)	_
C(6) - C(7)	1.445(3)	1.467(3)	
C(7) - C(8)	1.43(1)	1.643(2)	
C(8) - C(9)	1.42(1)	1.605(3)	
C(9) - C(22)	1.343(5)	1.337(4)	
S(2) - C(5)	1.726(3)	1.720(2)	1.723(1)
S(2) - C(6)	1.756(3)	1.744(2)	1.737(1)
C(4) - C(5)	1.415(3)	1.407(3)	1.416(2)
C(5) - C(11)	1.396(4)	1.394(3)	1.392(2)
C(11) - C(21)	1.407(3)	1.419(3)	1.422(2)
C(6) - C(21)	1.369(4)	1.360(3)	1.365(2)
N(1) - C(11)	1.391(3)	1.400(2)	1.393(2)
N(1) - C(13)	1.412(4)	1.497(3)	1.420(1)
C(7)-S(3)-C(22)	92.59(15)	95.35(15)	_ ``
S(3)-C(22)-C(9)	112.7(2)	116.8(2)	
C(8)-C(9)-C(22)	113.5(5)	116.8(2)	
C(7)-C(8)-C(9)	110.7(7)	93.79(14)	
S(3)-C(7)-C(6)	121.8(2)	120.98(17)	
C(5)-S(2)-C(6)	91.07(13)	90.77(10)	90.95(6)
S(2)-C(6)-C(21)	112.56(18)	112.83(16)	113.6(1)
S(2)-C(5)-C(11)	110.44(18)	111.72(15)	110.86(9)
C(6)-C(21)-C(11)	111.3(2)	111.97(18)	110.5(1)
C(5)-C(11)-C(21)	114.6(2)	112.71(17)	114.0(1)
C(11)-N(1)-C(19)	106.7(2)	106.54(15)	106.68(9)
N(1)-C(11)-C(5)	109.6(2)	109.14(17)	109.6(1)
C(4)-C(5)-C(11)	106.8(2)	107.42(17)	107.0(1)
<sup>a</sup> Ref. 21.			

bonds (*i.e.* C(9)–C(22) = 1.335 Å) in comparison to the parent thiophene (1.370 Å).<sup>34</sup> However, such shortening of external  $\alpha$ , $\beta$ -C–C bonds is typical of  $\alpha$ -oligothiophenes<sup>35</sup> and has been observed in previous DTP-based structures as well.<sup>18,19,21</sup>

The packing of **7b** consists of herringbone edge-to-face packed columns separated by the N-phenyl moieties (Fig. 4). The molecules are oriented with an interplanar angle of ~75° and each edge-to-face contact consists of two short S… $\pi$ contacts of 3.390 Å between the two central DTP units, as well as two additional C–H… $\pi$  contacts. The shorter C–H… $\pi$ contact (2.721 Å) occurs between a hydrogen on an external thiophene and the central DTP unit, while the longer contact (2.795 Å) is between two external thiophenes. In addition, each unit exhibits a third C–H… $\pi$  contact (2.868 Å) between the N-phenyl group and the DTP unit of a third **7b** molecule.



Fig. 4 Herringbone packing of 7b.

		Solution <sup>a</sup>			
Compound	$\lambda_{max}^{abs}$ (nm)	$\epsilon \; (M^{-1} \; cm^{-1})$	$\lambda_{max}^{em}$ (nm)	$\Phi_{\mathrm{F}}$	$\lambda_{max}^{abs}$ (nm)
<b>3a</b> <sup>b</sup>	310	26100	324	$7.78 \times 10^{-4}$	
3b	310	32 000			
$3c^c$	305	15400			
3d <sup>c</sup>	320	11 000			
$4^d$	390	34 700	$474^e$	0.16	331, (385), 450
<b>5</b> <sup>f</sup>	$408^{f}$		459, 486, $(522)^{g,h}$	$0.24^{g,h}$	340
<b>6</b> <sup><i>i</i></sup>	387 <sup>j</sup>		432, 455, $(486)^k$		344, 356
7a	400	56,000	440, 470, (506)	0.32	404. (434)
7b	396	45 100	444, (464)	0.70	409, (439)
8a	399	54 000	446, 468, (504)	0.68	417, (444)
8b	398	44 000	440, (467)	0.73	409, (430), (460)
<b>9</b> <sup><i>l</i></sup>	376 <sup>f</sup>	$35500^{f}$	$433, 455, (490)^{f}$	$0.29^{f}$	440
<b>10</b> <sup>m</sup>	389 <sup>f</sup>		$435^{h}$	$0.27^{h}$	
11	$369^{f,g}$		413, $432^n$		
12a	381	61 000	422, 442, (473)	0.53	393, (420)
12b	378	58 400	421, 440, (476)	0.87	354, (414)
$12c^{\circ}$	394 <sup>f</sup>	48 800			361
$12d^p$	$379^{h}$		423, $444^h$	$0.57^{h}$	400
13a	380	43 200	424, 439, (466)	0.62	406, 430
13b	380	45 500	424, (443)	0.92	381, (419)
<sup><i>a</i></sup> In CH <sub>3</sub> CN, val <sup><i>i</i></sup> Ref. 40. <sup><i>j</i></sup> In CH	lues in parentheses rep I <sub>2</sub> Cl <sub>2</sub> . <sup><i>k</i></sup> In C <sub>6</sub> H <sub>12</sub> . <sup><i>l</i></sup> Ref	present distinct shoulders. 7. 41. <sup>m</sup> Ref. 42. <sup>n</sup> Ref. 43.	<sup>b</sup> Ref. 18. <sup>c</sup> Ref. 19. <sup>d</sup> Ref. 1 <sup>o</sup> Ref. 23b. <sup>p</sup> Ref. 22b.	37. <sup>e</sup> Ref. 38. <sup>f</sup> In CHCl	<sup>g</sup> . <sup>g</sup> Ref. 39. <sup>h</sup> In THF.

Along the *b* axis, adjacent herringbone columns are interconnected by two additional types of C–H··· $\pi$  contacts, a DTP-terminal thiophene contact of 2.786 Å, as well as a phenyl-terminal thiophene contact of 2.889 Å.

### Absorption properties

Photophysical data for all of the DTP-based oligomers are given in Table 2 and representative UV-vis spectra of **7a**, **8a**, **12**, and **13a** are shown in Fig. 5. For comparison, data for the DTPs **3a–d**, the parent oligomers quaterthiophene (**4**) and 5,5-diphenyl-2,2'-bithiophene (**9**) and the fused-ring CPBT and DTT analogues (**5**, **6**, **10**, and **11**) are also included in Table 2.<sup>37–43</sup> Previous studies on oligothiophenes have shown that an increase in oligomer size, and thus conjugation length, results in a bathochromic shift in the absorption spectrum as well as an increase in the molar absorptivity.<sup>37</sup> As such, it is not surprising that all of the oligomers in Table 2 exhibit lower energy absorptions than their fused-ring bithienyl precursors (*i.e.* DTP, CTBT, or DTT).



Fig. 5 Representative UV-vis spectra in CH<sub>3</sub>CN.

The most dramatic trend within the oligomers investigated is the stark energetic difference in the absorbance of the thiophene-capped oligomers in comparison to their phenylcapped analogues. As shown in Fig. 5, the phenyl-capped oligomers exhibit a  $\sim 20$  nm blue-shift in comparison to the corresponding thiophene-capped analogues. This trend is consistent with the difference in the parent oligomers 4 and 9 and can be at least partially attributed to increased steric interactions between the phenyl group and the bithienyl core. This is in line with the more distorted geometry calculated for the phenyl-capped DTPs in comparison to their thienylsubstituted analogues (i.e., DFT modeling of thiophene- and phenyl-capped DTPs reveal that the torsional angles between the terminal external rings and the DTP unit are  $\sim 7^{\circ}$  greater for phenyl end-capped than for their thienyl end-capped analogues, see supporting information). Another additional factor here is the increased electron confinement in the more aromatic benzene in comparison to that of thiophene.<sup>44</sup>

In terms of N-functionalization effects, previous studies of DTP monomers have shown that N-alkyl- and N-aryl-DTPs exhibit similar  $\lambda_{max}$  values for the lowest energy transition. However, the additional conjugation of the N-aryl group results in broadening of this transition and thus a slightly red-shifted onset of absorption ( $\sim 5-10$  nm).<sup>18,28</sup> Comparing N-alkyl- to N-acyl-DTPs again show significant broadening of the low energy transitions of the N-acylDTPs and an even greater red-shift for the absorption onset ( $\sim 20$  nm). It has been proposed that the lowest energy transition of the N-acylDTPs exhibits some charge transfer (CT) character due to the fact that the N-acyl group does not contribute to the DTP HOMO, but does contribute to the LUMO.<sup>19</sup> This CT nature thus accounts for the observed broadening and red-shifted absorption. The combination of aryl and acyl functionality in N-benzoyl side chains resulted in the greatest observed red-shifts.

Oligomer	E <sub>max</sub> (eV)	f	Description
7a	2.96	1.29	$HOMO \rightarrow LUMO (99\%)$
7b	2.97	1.24	$HOMO \rightarrow LUMO(99\%)$
8a	2.87	1.08	$HOMO \rightarrow LUMO (98\%)$
8b	2.73	0.37	$[HOMO \rightarrow LUMO] (77\%) + [HOMO \rightarrow LUMO + 1] (20\%)$
12a	3.21	1.31	$HOMO \rightarrow LUMO (98\%)$
12b	3.23	1.24	HOMO $\rightarrow$ LUMO (98%)
13a	3.11	1.03	HOMO $\rightarrow$ LUMO (98%)
13b	2.87	0.22	$[HOMO \rightarrow LUMO] (77\%) + [HOMO \rightarrow LUMO + 1] (15\%)$

 Table 3 Results of TDDFT//B3LYP/6-31G\*\* calculations for the DTP-based oligomers

It could be expected that the same trends in N-functionalization effects would carry over to the corresponding DTP-based oligomers. However, as illustrated by the solution absorption data in Table 2 and Fig. 5, this does not seem to be the case. All of the investigated oligomers exhibit spectra with nearly identical absorption profiles ( $\lambda_{max}$  shifts of ~4 nm or less and nearly identical absorption onsets), with the only deviation being that the N-acyl-functionalized oligomers exhibit near 300 nm. To make these observations even more perplexing, the side chains that gave red-shifts in the DTP monomers actually produced slight blue-shifts in the corresponding oligomers, and thus the *N*-alkylDTP oligomers gave the lowest energy  $\lambda_{max}$  values.

To investigate the optical properties of the DTP-based oligomers, the lowest-energy electronic excited states were calculated using the time-dependent DFT (TDDFT) approach (see Table 3). The calculated transition energies, although slightly red-shifted, are in good agreement with the experimental values.

For all the DTP-based oligomers, the most intense lowestenergy electronic excitation is mainly attributed to a oneelectron excitation from the HOMO to the LUMO. As previously seen for N-alkyl-18 and N-acyl-DTPs19 and the DTP-based oligomer 7c,<sup>21</sup> both the HOMO and LUMO are of  $\pi$  nature and mainly spread over the entire conjugated backbone with no contribution from the N-alkyl or N-aryl groups (see Fig. 6), although significant electron density is found on the N-acyl group. The observed blue-shift in absorption for the phenylcapped oligomers is well reproduced by the theoretical calculations (i.e., the excitation energy is calculated to increase by 0.25 eV on going from 7a and 12a). However, theoretical calculations predict a red-shift of the lowest energy absorption upon replacing N-alkyl or N-aryl groups with N-acyl (i.e., 3.21 eV in 8a and 3.11 eV 13a), which is in line with the experimental trend previously found for the DTP monomers.

The deviation of the solution absorption data from the trend previously observed from the monomeric DTPs could be explained by different degrees of rotational disorder among the various DTP-based oligomers investigated. It is understood that conjugated oligomers and polymers adopt a nonplanar, or coiled, conformation in solution,45-47 providing that interannular rotations between units are possible. It is theorized that the extent of this disorder (or deviation from planarity) reflects a competition between solvation energy, largely influenced by the polarizability of the conjugated species, and the energy of the rotational conformation.<sup>45</sup> The extent of conjugation influences the polarizability of the backbone, and thus the solvation energy. As such, the solvent-oligomer interactions determine the optimal backbone conformation and therefore the extent of conjugation in solution. While changes in typical side chains should have little effect on polarizability, the addition of the N-acyl groups directly affect the electronic nature of the oligomer and could thus contribute to changes in polarizability. As a result, the solution conformation of the N-acyl oligomers could be very different than the N-alkyl analogues, thus resulting in attenuation of the full conjugation length which would account for the lack of red-shift in the spectra as initially expected.

In an attempt to verify this theory, the absorption properties of the DTP-based oligomers were also examined as spin-cast thin films. As solid-state films, the solvent interactions are removed and the oligomers would be expected to adopt more planar conformations with maximized conjugation lengths. As shown in Fig. 7, the solid-state spectra now follow the trends experimentally observed in their parent monomers and those as predicted by theoretical calculations. It can therefore be shown that for conjugated backbones beyond the monomers, alkyl *vs.* aryl side chains have little effect on the absorption properties, while acyl and benzoyl groups both give respective shifts to lower energy.



Fig. 6 Electronic density contours, calculated at B3LYP/6-31G\*\* level, for the HOMO and LUMO frontier molecular orbitals of **7a** and **8a**.



Fig. 7 Solid-state absorption spectra of DTP-based quaterthiophenes.

The lack of correlation between the solution data and the predicted structure-function relationships for these oligomers is an excellent example of the complexity of determining such relationships by utilizing solution data alone. The greater understanding of the competing effects involved in determining the solution absorption properties of these DTP-based oligomers now accounts for some of the previously unexplained inconsistencies found in comparing solution data of seemingly similar oligomers.<sup>21,23a</sup>

### Solution emission properties

Oligomers containing DTP cores have been previously shown to exhibit quite strong fluorescence in comparison to typical oligothiophenes<sup>20,21</sup> and thus one of the primary goals of the current study was to further understand how to enhance fluorescence in these systems *via* molecular tuning. The emission energies and quantum yields ( $\Phi_F$ ) for the full series are collected in Table 2 and representative emission spectra of the DTP-based oligomers **7a**, **8a**, **12a**, and **13a** are shown in Fig. 8. For all oligomers, the observed emission spectra are essentially identical to the parents **4**<sup>37</sup> or **9**<sup>41</sup> in both energy and structure. The observed structured emission are characteristic of a planar excited state and is consistent with the planar quinoid-like structure proposed for the singlet excited state of oligothiophenes.<sup>48</sup> The vibrational spacings are ~1100–1500 cm<sup>-1</sup>, which correspond well with the ring-breathing modes of thiophene and pyrrole.<sup>49</sup>

As with the absorption data discussed above, the reduced conjugation of the phenyl-capped oligomers causes a blue-shift of  $\sim 20$  nm in the emission in comparison to the thiophenecapped analogues. However, this increase in energy is offset by a significant increase in quantum efficiency. This enhanced emission is consistent with other phenyl-containing oligothiophenes<sup>41</sup> and can be attributed to the fact that reduced thiophene content lessens spin–orbit coupling as a consequence of the heavy atom affect. As a result, lower triplet quantum yields reduce loss *via* non-radiative processes from the triplet state.<sup>21</sup>

In terms of N-functionalization effects, oligomers containing simple alkyl side chains (**7a** and **12a**) exhibit the lowest quantum yields within the DTP-based series. However, these lower efficiencies are still higher than any of the other analogous oligomers without DTP cores. The enhanced emission of DTP-based oligomers has been previously attributed to its ring fusion, which reduces low frequency, interannular torsional vibrations responsible for non-radiative deactivation,<sup>50,51</sup> and the photochemical stability



Fig. 8 Representative emission spectra in CH<sub>3</sub>CN.

of DTP in comparison to other fused-ring units such as CPBT.<sup>21</sup> The application of saturated alkyl side chains such as the N-octyl groups in **7a** and **12a** add high frequency modes which can result in a greater number of deactivation pathways *via* internal conversion, contributing to reductions in  $\Phi_{\rm F}$ .<sup>10,52</sup> These modes increase with the number of methylene units on the alkyl chain and it has been previously shown that the application of smaller alkyl groups results in significantly higher efficiencies ( $\Phi_{\rm F} = 0.65$  for **7c** in CH<sub>3</sub>CN).<sup>21</sup> The lack of such high frequency modes in the N-phenyl derivatives also accounts for the large increase in  $\Phi_{\rm F}$  for **7b** and **12b**.

Somewhat unexpectedly, the application of N-acyl groups also results in large increases in fluorescence efficiency. The N-octanoyl groups of 8a and 13a do have one less methylene unit in comparison to the N-octyl groups of 7a and 12a, but this is not enough to account for the large difference in  $\Phi_{\rm F}$ . The addition of carbonyl groups to oligothiophenes has previously been shown to reduce non-radiative decay and increase  $\Phi_{\rm F}$ .<sup>53,54</sup> In these cases, it was proposed that this was due to an increase in conjugation, which is known to decrease intersystem crossing and thus reduce non-radiative decay via vibrational relaxation from the triplet state.<sup>37</sup> Nevertheless, a doubling of  $\Phi_{\rm F}$  has been shown to be possible by application of the acyl group to DTP-based oligomers. The gains in efficiency are greatest in oligomers initially exhibiting weaker fluorescence (7a to 8a), although smaller increases are still seen even for stronger emitters (12a to 13a). Although the N-benzoyl oligomers 8b and 13b both exhibit strong emission, particular care had to be made to remove an unknown trace impurity that, when present, quenched the fluorescence in these species.

### Electrochemistry

In order to determine the effect of molecular structure on the HOMO, the electrochemistry of the DTP-based oligomer series was investigated by cyclic voltammetry (CV). The representative voltammogram of **7a** is shown in Fig. 9 and the CV data for the full series is collected in Table 4. All oligomers exhibit an initial well-defined, quasi-reversible redox couple followed by a second irreversible oxidation. This electrochemical behaviour agrees well with that previously reported for the analogous phenyl-capped species **12e**<sup>23b</sup> and **12d**,<sup>22b</sup> although the second oxidation was not observed in the case of **12c**.

While not that surprising for the phenyl-capped oligomers,<sup>55</sup> the reversibility of the initial oxidation is somewhat unusual for an oligothiophene. For typical oligothiophenes, oxidation results in the formation of a radical cation with significant radical density on the  $\alpha$ -positions of the external thiophenes. As such, these oxidations are typically irreversible due to rapid coupling of the



Fig. 9 Cyclic voltammogram of 7a.

 Table 4
 Cyclic voltammetry data for DTP oligomers<sup>a</sup>

			0.0	
Oligomer	$E_{1/2}^{0/+1}(V)$	$\Delta E (\mathrm{mV})$	$E_{pa}^{+1/+2}(V)$	$E_{HOMO} (eV)^b$
7a	0.30	100	0.93	-5.29
7b	0.36	80	1.06	-5.35
12a	0.38	80	1.05	-5.37
12b	0.47	80	1.09	-5.45
12c <sup>c</sup>	0.36			$-5.40^{d}$
12d <sup>e</sup>	0.49	180	1.31	-5.43
8a	0.47	100	0.86	-5.43
8b	$0.51^{f}$		1.09	-5.46
13a	0.58	60	1.13	-5.56
13b	0.62	80	1.13	-5.60

<sup>*a*</sup> Potential *vs.* Ag/Ag<sup>+</sup> measured in millimolar argon-sparged CH<sub>3</sub>CN solutions with 0.10 M TBAPF<sub>6</sub> as supporting electrolyte. <sup>*b*</sup> E<sub>HOMO</sub> =  $-(E_{\text{[onset,ox vs. Fc+/Fc]}} + 5.1)(\text{eV})$ . <sup>*c*</sup> Ref. 23*b*, in CH<sub>2</sub>Cl<sub>2</sub>, second oxidation not observed. <sup>*d*</sup> Determined from E<sub>1/2</sub>, rather than onset. <sup>*e*</sup> Ref. 22*b*, in CH<sub>2</sub>Cl<sub>2</sub>. <sup>*f*</sup> Irreversible oxidation, E<sub>pa</sub> is reported.

radical cations resulting in larger oligomeric or polymeric species.<sup>56</sup> For the DTP-based oligothiophenes here, however, it is possible to cycle repeatedly through the first redox couple with no change in electrochemistry and no detectable coupling.

In order to further investigate this unusual behaviour, the electron spin density was calculated for the radical cation of **7a** (see supporting information). While the calculated spin-density contour was delocalized over the full oligomer backbone, the density profile revealed that 62% of the unpaired spin was localized on the central DTP unit, with only 14% of the spin on each of the  $\alpha$ -positions of the external thiophenes. Thus, coupling of the radical cation may be possible at either lower scan rates or if the potential was held after the initial oxidation, but was not observed at a scan rate of 100 mV s<sup>-1</sup>. Coupling and the generation of polymeric material was observed to occur fairly rapidly if cycling was carried out to potentials beyond the second oxidation. The fact that coupling occurs after the second oxidation, rather than a simple dication.

As can be seen in Table 4, it is possible to tune the energy of the HOMO by over 300 mV through a combination of the choice of aryl end-cap and N-functionalization. Not surprisingly, the lower conjugation of the phenyl-capped oligomers results in stabilization of the HOMO by  $\sim 80-110$  mV in comparison to the analogous thienyl-capped oligomers. However, the choice of N-functionalization also results in significant modulation of the HOMO energy, with stabilization increasing in the following order: N-alkyl < N-aryl < N-acyl < N-benzoyl. Thus the combination of N-benzoyl groups with external phenyl groups gives the most stabilized HOMOs, while N-alkyl groups and thiophene end-caps give the most destabilized HOMOs.

Ionization potentials (IPs) are calculated at both Koopmans' theorem<sup>57</sup> (KT) and self-consistent-field ( $\Delta$ SCF) levels (see Fig. 10 and supporting information). It is found that the trends in the vertical IPs and the calculated HOMO values are very similar; that is, Koopmans' theorem (where IP =  $-E_{HOMO}$ ) applies well. In agreement with the higher oxidation potentials obtained for phenyl end-capped oligomers in comparison to their thienyl analogues, larger IP values and more stabilized HOMO levels are found (*i.e.*, the vertical IP is estimated to be 6.01 eV in **7a** and 6.11 eV in **12a**). DFT-calculated IP values also nicely predict



Fig. 10 DFT-calculated HOMO levels (in absolute values) and vertical ionization potentials (IPs) for DTP-based oligomers. The experimental potential values for the first oxidations are included for comparison.

the large HOMO stabilization experimentally observed upon N-acyl substitution; for instance, the IP value increase by 0.25 eV on going from N-alkyl-substituted **7a** to the analogous N-acyl-substituted **8a**. The combined experimental and computational results clearly show that the high lying HOMO thought to be a limitation in some DTP-based materials can be overcome through application of the new *N*-acylDTP building blocks.

# **Experimental methods**

Unless noted, all materials were reagent grade and used without further purification. N-OctyIDTP 3a,<sup>26</sup> N-acyIDTPs 3c,d,<sup>17</sup> oligomer 7a,<sup>21</sup> and 2-(tributylstannyl)thiophene<sup>58</sup> were prepared according to previously reported literature procedures. Dry THF and toluene were obtained via distillation over sodium/ benzophenone. All glassware was oven-dried, assembled hot, and cooled under a dry nitrogen stream before use. Transfer of liquids was carried out using standard syringe techniques and all reactions were performed under dry nitrogen. Chromatographic separations were performed using standard column chromatography methods with silica gel (230-400 mesh). Melting points were determined using a digital thermocouple with 0.1 °C resolution. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on a 400 MHz spectrometer. All NMR data are referenced to the chloroform signal and peak multiplicity reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet,m = multiplet and br = broad. HRMS (ESI) was performed in house.

### *N*-Phenyldithieno[3,2-*b*:2',3'-*d*]pyrrole (3b)

DTP **3b** was prepared using previously reported methods,<sup>59</sup> substituting <sup>1</sup>Bu<sub>3</sub>P with BINAP. The crude product was purified *via* column chromatography in hexanes, producing a white solid (87%). mp 125.4–126.1 °C; <sup>1</sup>H NMR  $\delta$ : 7.58 (m, 4H), 7.50 (m, 3H), 7.31 (m, 2H); <sup>13</sup>C NMR  $\delta$ : 144.3, 141.2, 137.8, 129.9, 123.6, 122.8, 116.9, 112.6; HRMS: *m/z* 256.0242 [M+] (calcd for C<sub>14</sub>H<sub>9</sub>NS<sub>2</sub> 256.0249).

### General procedure for synthesis of 2,6-distannylDTPs

The desired DTP (2.08 mmol) was combined with dry hexane (60 mL) and the solution cooled to 0  $^\circ$ C. TMEDA

(0.89 mL, 6.0 mmol) was added, followed by BuLi (2.5 M in hexanes, 2.4 mL, 6.0 mmol) and the mixture stirred for 2 h. Me<sub>3</sub>SnCl (1.0 M in THF, 6.0 mL, 6.0 mmol) was then added and the solution stirred overnight. This was then poured over  $Et_3N$ -treated silica gel, filtered, and rinsed with hexane. The filtrate was concentrated *via* rotary evaporation and then pumped overnight. The product was stored under  $N_2$  in the freezer until further use.

# *N*-Octyl-2,6-bis(trimethylstannyl)dithieno[3,2-*b*:2',3'-*d*]pyr-role (14a)

Isolated as a pale yellow oil (99% yield). <sup>1</sup>H NMR:  $\delta$  7.00 (s, 2H), 4.18 (t, J = 7.2 Hz, 2H), 1.88 (p, J = 7.2 Hz, 2H), 1.35 (m, 2H), 1.27 (m, 8H), 0.87 (t, J = 7.2 Hz, 3H), 0.40 (s, 18H); <sup>13</sup>C NMR:  $\delta$  148.1, 131.4, 120.8, 118.2, 47.7, 32.1, 30.7, 29.4, 28.7, 27.3, 22.9, 14.3, -7.9.

## *N*-phenyl-2,6-bis(trimethylstannyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole (14b)

Isolated as an orange solid (99% yield). mp 131.8 °C (dec); <sup>1</sup>H NMR:  $\delta$  7.63 (m, 2H), 7.54 (m, 2H), 7.33 (m, 1H), 7.17 (s, 2H), 0.40 (s, 18H); <sup>13</sup>C NMR:  $\delta$  147.1, 140.3, 136.9, 130.0, 125.9, 123.0, 122.8, 119.3, -7.9.

## General procedure for synthesis of *N*-alkyl- and *N*-aryl-DTPbased oligomers

To a 60 mL Shlenk tube was added the desired intermediate **14** (0.50 mmol),  $Pd_2dba_3$  (0.01 g, 0.01 mmol), and  $P(o-tolyl)_3$  (0.01 g, 0.04 mmol). The Schlenk tube was evacuated and backfilled with N<sub>2</sub> three times. Degassed toluene (10 mL) was then added followed by either bromobenzene or 2-bromothiophene (1.1 mmol). The reaction was heated with stirring at 95 °C until completion (*ca.* 24 h). Water was added and the mixture extracted with CHCl<sub>3</sub>. The combined organic layers were dried with MgSO<sub>4</sub> and concentrated *via* rotary evaporation to give the crude product which was purified *via* column chromatography (2% EtOAc in hexane).

### *N*-Phenyl-2,6-bis(2-thienyl)dithieno[3,2-b:2'3'-d]pyrrole (7b)

81%; mp 193.5 °C (dec); <sup>1</sup>H NMR:  $\delta$  7.60 (m, 4H), 7.39 (m, 1H), 7.21 (m, 6H), 7.03 (m, 2H); <sup>13</sup>C NMR:  $\delta$  144.9, 142.1, 138.7, 135.8, 130.2, 128.1, 126.7, 124.4, 123.5, 123.2, 116.2, 108.8; HRMS: *m*/*z* 418.9931 [M+] (calcd for C<sub>22</sub>H<sub>13</sub>NS<sub>4</sub> 418.9925).

### *N*-Octyl-2,6-diphenyldithieno[3,2-*b*:2',3'-*d*]pyrrole (12a)

66%; mp 102.0–102.6 °C; <sup>1</sup>H NMR:  $\delta$  7.66 (d, J = 7.5 Hz, 4H), 7.40 (t, J = 7.5 Hz, 4H), 7.28 (t, J = 7.5 Hz, 2H), 7.27 (s, 2H), 4.32 (t, J = 7.0 Hz, 2H), 1.93 (p, J = 7.0 Hz, 2H), 1.30 (m, 10H), 0.87 (t, J = 6.0 Hz, 3H); <sup>13</sup>C NMR:  $\delta$  144.9, 142.1, 136.0, 129.2, 127.4, 125.6, 119.1, 107.2, 47.7, 32.0, 30.6, 29.4, 29.3, 27.3, 22.8, 14.3; HRMS: m/z 443.1733 [M+] (calcd for C<sub>28</sub>H<sub>29</sub>NS<sub>2</sub> 443.1736).

### *N*-Phenyl-2,6-diphenyldithieno[3,2-*b*:2',3'-*d*]pyrrole (12b)

41%; mp 212.6 °C (dec); <sup>1</sup>H NMR:  $\delta$  7.64 (m, 6H), 7.58 (m, 2H), 7.40 (s, 2H), 7.39 (m, 5H), 7.27 (m, 2H); <sup>13</sup>C NMR:  $\delta$  144.2, 142.9, 139.9, 135.6, 130.2, 129.2, 127.6, 126.6, 125.6,

123.2, 116.8, 108.3; HRMS: m/z 407.0807 [M+] (calcd for C<sub>26</sub>H<sub>17</sub>NS<sub>2</sub> 407.0797).

# General procedure for the bromination of N-acylDTPs

In a 3-necked flask, the desired *N*-acylDTP (2.31 mmol) was dissolved in 20 mL of dry CHCl<sub>3</sub>. The flask was equipped with an addition funnel and wrapped in Al foil in order to reduce exposure to light. A solution of NBS (0.90 g, 5.08 mmol) in 20 mL MeCN was cooled to 0 °C and then added dropwise *via* the addition funnel. The reaction was allowed to stir overnight, after which water was added and the mixture was extracted with CHCl<sub>3</sub>. The combined organic layers were dried with MgSO<sub>4</sub>, filtered, and concentrated *via* rotary evaporation. The crude solid was then placed in boiling hexanes, filtered hot, and allowed to recrystallize producing a light brown solid.

# 2,6-Dibromo-N-octanoyldithieno[3,2-b:2',3'-d]pyrrole (15a)

85%; mp 98.9–99.3 °C; <sup>1</sup>H NMR: δ 7.52 (br, 2H), 2.93 (t, J = 7.2 Hz, 2H), 1.85 (p, J = 7.6 Hz, 2H), 1.37 (m, 8H), 0.90 (t, J = 7.0 Hz, 3H). <sup>13</sup>C NMR: δ 169.4, 142.1, 137.5, 119.8, 111.9, 36.5, 31.9, 29.4, 24.3, 22.9, 14.3; HRMS: m/z 462.9101 [M+] (calcd for C<sub>16</sub>H<sub>17</sub>NOS<sub>2</sub>Br<sub>2</sub> 462.9092).

# *N*-Benzoyl-2,6-dibromodithieno[3,2-*b*:2',3'-*d*]pyrrole (15b)

70%; mp 184.8–186.2 °C; <sup>1</sup>H NMR:  $\delta$  7.70 (m, 4H), 7.58 (tt, J = 7.2, 0.4 Hz, 1H), 6.88 (s, 2H); <sup>13</sup>C NMR:  $\delta$  167.0, 143.1, 134.5, 132.6, 129.1, 129.3, 121.8, 119.3, 111.7.

# General procedure for synthesis of *N*-acylDTP-based oligomers *via* Stille cross-coupling

To a 60 mL Shlenk tube was added the desired intermediate **15** (1.00 mmol), 2-(tributylstannyl)thiophene (0.82 g, 2.20 mmol),  $Pd_2dba_3$  (0.02 g, 0.02 mmol), and P(o-tolyl)<sub>3</sub> (0.02 g, 0.08 mmol). The Shlenk tube was evacuated and backfilled with N<sub>2</sub> three times. Degassed toluene (12 mL) was then added and the reaction heated with stirring at 95 °C until completion (*ca.* 24 h). Water was added and the mixture extracted with CHCl<sub>3</sub>. The combined organic layers were dried with MgSO<sub>4</sub> and concentrated *via* rotary evaporation to give the crude product which was purified *via* column chromatography (5% EtOAc in hexane).

# *N*-Octanoyl-2,6-bis(2-thienyl)dithieno[3,2-b:2'3'-d]pyrrole (8a)

47%; mp 138.6–139.3 °C; <sup>1</sup>H NMR:  $\delta$  7.57 (br s, 2H), 7.25 (dd, J = 3.6, 1.2 Hz, 2H), 7.23 (dd, J = 3.6, 0.8 Hz, 2H), 7.05 (t, J = 3.6 Hz, 2H), 3.02 (t, J = 7.2 Hz, 2H), 1.90 (p, J = 7.6 Hz, 2H), 1.52 (m, 2H), 1.38 (m, 6H), 0.91 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR:  $\delta$  169.7, 144.7, 139.1, 135.1, 128.2, 125.0, 123.9, 114.1, 107.7, 36.7, 32.0, 29.5, 29.4, 24.4, 22.9, 14.3; HRMS: m/z 469.0651 [M+] (calcd for C<sub>24</sub>H<sub>23</sub>NOS<sub>2</sub> 469.0657).

# *N*-Benzoyl-2,6-bis(2-thienyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole (8b)

37%; mp 151.2–152.0 °C; <sup>1</sup>H NMR:  $\delta$  7.77 (d, J = 6.4 Hz, 2H), 7.71 (t, J = 5.8 Hz, 1H), 7.59 (t, J = 6.2 Hz, 2H), 7.21 (d, J = 4.0 Hz, 2H), 7.14 (d, J = 2.4 Hz, 2H), 7.01 (t, J = 3.4 Hz, 2H), 6.91 (s, 2H); <sup>13</sup>C NMR  $\delta$ : 169.9, 145.2, 142.4, 138.1, 136.7, 134.3, 132.6, 129.1, 128.9, 128.2, 124.9, 123.8, 112.9; HRMS: m/z 446.9887 [M+] (calcd for C<sub>23</sub>H<sub>13</sub>NOS<sub>4</sub> 446.9874).

# General procedure for synthesis of *N*-acylDTP-based oligomers via Suzuki cross-coupling

To a 60 mL Shlenk tube was added the desired intermediate **15** (0.412 mmol), phenyl boronic acid (0.110 g, 0.906 mmol), and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.014 g, 0.021 mmol). The tube was then evacuated and backfilled with N<sub>2</sub> three times. Degassed toluene (20 mL) was then added, followed by a degassed solution of K<sub>2</sub>CO<sub>3</sub> in water (1.0 mL, 1.6 M). The reaction was then heated with stirring at 95 °C until completion (*ca.* 24 h). Water was added and the mixture extracted with CHCl<sub>3</sub>. The combined organic layers were dried with MgSO<sub>4</sub> and concentrated *via* rotary evaporation to give the crude product which was purified *via* column chromatography (5% EtOAc in hexane).

### N-Octanoyl-2,6-diphenyldithieno[3,2'b:2',3'-d]pyrrole (13a)

32%; <sup>1</sup>H NMR:  $\delta$  7.63 (d, J = 7.2 Hz, 2H), 7.54 (br s, 2H), 7.41 (t, J = 7.6 Hz, 4H), 7.31 (t, J = 7.4 Hz, 4H), 2.99 (t, J =7.2 Hz, 2H), 1.88 (p, J = 7.2 Hz, 2H), 1.43 (m, 8H), 0.90 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR:  $\delta$  169.9, 144.9, 142.2, 136.3, 129.3, 128.2, 125.8, 120.2, 108.3, 36.6, 31.9, 29.5, 29.4, 24.4, 22.9, 14.3; HRMS: m/z 480.1460 [M+] (calcd for C<sub>28</sub>H<sub>27</sub>NOS<sub>2</sub> 480.1426).

### N-Benzoyl-2,6-diphenyldithieno[3,2-b:2',3'-d]pyrrole (13b)

68%; mp 179.8–180.0 °C; <sup>1</sup>H NMR: δ 7.80 (d, J = 5.6 Hz, 2H), 7.72 (t, J = 5.8 Hz, 1H), 7.60 (t, J = 6.2 Hz, 2H), 7.52 (d, J = 6.0 Hz, 4H), 7.37 (t, J = 6.2 Hz, 4H), 7.28 (t, J = 6.4 Hz, 2H), 7.08 (s, 2H); <sup>13</sup>C NMR δ: 169.9, 144.3, 143.7, 142.9, 135.0, 134.7, 132.5, 129.3, 129.1, 129.0, 127.9, 125.7, 112.4; HRMS: m/z 435.0760 [M+] (calcd for C<sub>27</sub>H<sub>17</sub>NOS<sub>2</sub> 435.0746).

### X-ray diffraction

X-ray quality crystals of **3b** and **7b** were grown by the slow evaporation of isopropanol solutions. Crystals of **15a** were grown from hexane solutions. The X-ray intensity data of the crystals were measured at 100 K on a Bruker Kappa Apex II Duo CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ( $\lambda = 0.71073$  Å) operated at 2000 W of power. The detector was placed at a distance of 5.000 cm from the crystal and data collected *via* the Bruker APEX2 software package. The frames were integrated with the Bruker SAINT software package. The unit cell was determined and refined by least-squares upon the refinement of XYZ-centeroids of reflections above  $20\sigma(I)$ . The structure was refined using the Bruker SHELXTL (Version 5.1) Software Package.

### Crystal data for 3b

 $C_{14}H_9NS_2$ , M = 255.34, monoclinic, a = 9.9552(11), b = 14.2894(16), c = 8.1057(9) Å, V = 1128.8(2) Å<sup>3</sup>, T = 100 K, space group  $P2_1/c$ , Z = 4, 9952 reflections measured, 2707 unique ( $R_{int} = 0.0167$ ) which were used in all calculations. The final  $wR_2$  was 0.0721 (all data).

### Crystal data for 7b

 $C_{22}H_{13}NS_4$ , M = 419.57, orthorhombic, a = 10.8666(3), b = 22.8858(6), c = 7.4246(2) Å, V = 1846.43(9) Å<sup>3</sup>, T = 100 K, space group Pna2(1), Z = 4, 6775 reflections measured, 2525 unique ( $R_{int} = 0.0292$ ) which were used in all calculations. The final  $wR_2$  was 0.0809 (all data).

## Crystal data for 15a

 $C_{16}H_{17}Br_2NOS_2$ , M = 463.25, mono-clinic, a = 8.9068(6), b = 21.4647(14), c = 9.5892(6) Å, V = 1736.2(2) Å<sup>3</sup>, T = 100 K, space group  $P2_1/c$ , Z = 4, 15 990 reflections measured, 4003 unique ( $R_{int} = 0.0229$ ) which were used in all calculations. The final  $wR_2$  was 0.0429 (all data).

### Theoretical methodology

Calculations were performed with the Gaussian 03 program.<sup>60</sup> The molecular geometries of the neutral and radical-ion states were calculated at the DFT level using the B3LYP functional<sup>61,62</sup> and the 6-31G\*\* basis set.<sup>63–65</sup> For all model oligomers, alkyl groups were shortened to save computational time. The time-dependent DFT (TDDFT) approach was used for the evaluation of the energies of the lowest singlet excited states.<sup>66</sup> The ionization potentials (IPs) and electron affinities (EAs) were calculated directly from the relevant points on the potential energy surfaces using the standard procedure detailed in the literature.<sup>67</sup>

### Preparation of thin films for solid-state spectroscopy

Oligomer thin films were prepared by spin-casting from saturated oligomer solutions in CHCl<sub>3</sub>. The solutions were then loaded onto clean glass substrates ( $\sim 1 \times 2$  cm) and spun at 1000 RPM for 60 s.

### Absorption and emission spectroscopy

UV-vis spectroscopy was performed on a dual beam scanning UV-vis-NIR spectrophotometer using samples prepared as dilute CH<sub>3</sub>CN solutions in quartz cuvettes or as thin films on glass slides. Spectroscopy solvents were dried over molecular sieves prior to use. Solid-state absorption spectroscopy was conducted on thin films on glass substrates.

Emission spectroscopy was performed using dilute, deoxygenated CH<sub>3</sub>CN solutions at room temperature. Quantum yields were determined using secondary methods with 9,10-diphenylanthracene in deoxygenated cyclohexane as the reference.<sup>68</sup> Prior to each fluorescence measurement, the absorption spectrum was measured to ensure that the maximum absorption of the solution was less than 0.1. As the oligomer data was collected in CH<sub>3</sub>CN, corrections for the difference in the solvent refractive indices were applied using the following values: 1.426 for cyclohexane, and 1.350 for CH<sub>3</sub>CN.

### Electrochemistry

All electrochemical methods were performed utilizing a threeelectrode cell consisting of platinum disc working electrode, a platinum wire auxiliary electrode, and a Ag/Ag<sup>+</sup> reference electrode (0.251 V vs. SCE).<sup>69</sup> Supporting electrolyte consisted of 0.10 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in dry CH<sub>3</sub>CN. Solutions were deoxygenated by sparging with argon prior to each scan and blanketed with argon during the measurements. All measurements were collected at a scan rate of 100 mV s<sup>-1</sup>. E<sub>HOMO</sub> values were estimated from the onset of oxidation in relation to ferrocene (50 mV vs. Ag/Ag<sup>+</sup>), using the value of 5.1 eV vs. vacuum for ferrocene.<sup>70</sup> The molecular tuning effects of both aryl endgroups (thienyl vs. phenyl) and N-functionalities (alkyl, aryl, acyl, benzoyl) on DTP-based oligomers has been fully characterized via optical spectroscopy, electrochemistry, and DFT calculations. As previously seen in related materials, DTP oligomers end-capped with thienyl groups gave longer wavelength absorption and emission in comparison to their phenyl end-capped analogues. In solution, no obvious effect was seen in the absorption spectra from changes in N-functionalities, which was proposed to be due to differences in solution conformation. As solid-state films, however, side chain dependent red-shifts in absorption were observed in the following order:  $alkyl \sim aryl < acyl < benzoyl$ . In addition, significant enhancements in fluorescence efficiencies were observed for oligomers containing aryl end-groups or aryl/ acyl N-functionalities. These effects were found to be additive, with the greatest enhancement from the combination of aryl end-groups with acvl or arvl side chains. Lastly, it was found that the HOMO energies can be stabilized either by the application of aryl end-groups instead of thienyl end-groups or by the choice of N-functionalization, with stabilization increasing in the order N-alkyl < N-aryl < N-acyl < N-benzoyl. Thus the combination of N-benzoyl with external phenyl groups gives the most stabilized HOMOs. In conclusion, the results presented herein strongly illustrate the ability to tune the optical and electronic properties of DTP-based materials not only *via* backbone modification, but through the choice of N-functionalization of the DTP unit applied.

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## Notes and references

- T. P. Nguyen and P. Destruel, in *Handbook of Luminescence*, *Display Materials, and Devices*, ed. H. S. Nalwa and L. S. Rohwer, American Scientific Publishers, Stevenson Ranch, CA, 2003, Vol. 1, p. 5.
- 2 Handbook of Conducting Polymers, ed. T. A. Skotheim and J. R. Reynolds, CRC Press, Boca Raton, FL, 3rd edn, 2007.
- 3 S. C. Rasmussen, K. Ogawa and S. D. Rothstein, in *Handbook of Organic Electronics and Photonics*, ed. H. S. Nalwa, American Scientific Publishers, Stevenson Ranch, CA, 2008, Vol. 1, Ch 1.
- 4 Handbook of Oligo- and Polythiophenes, ed. D. Fichou, Wiley-VCH, Weinheim, 1999.

- 5 A. Mishra, C.-Q. Ma, J. L. Segura and P. Bäuerle, in *Handbook of Thiophene-based Materials*, ed. I. F. Perepichka and D. F. Perepichka, John Wiley & Sons, Hoboken, 2009.
- 6 T. Izumi, S. Kobashi, K. Takimiya, Y. Aso and T. Otsubo, J. Am. Chem. Soc., 2003, **125**, 5286–5287.
- 7 N. Sumi, H. Nakanishi, S. Ueno, K. Takimiya, Y. Aso and T. Otsubo, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 979.
- 8 J. G. Laquindanum, H. E. Katz and A. J. Lovinger, *J. Am. Chem. Soc.*, 1998, **120**, 664.
- 9 Z. Bao, Adv. Mater., 2000, 12, 227.
- 10 G. Barbarella, L. Favaretto, G. Sotgiu, M. Zambianchi, V. Fattori, M. Cocchi, F. Cacialli, G. Gigli and R. Cingolani, *Adv. Mater.*, 1999, **11**, 1375.
- 11 U. Mitschke and P. Bäuerle, J. Chem. Soc., Perkin Trans. 1, 2001, 740.
- 12 U. Mitschke, E. Mena Osteritz, T. Debaerdemaeker, M. Sokolowski and P. Bäuerle, *Chem.-Eur. J.*, 1998, 4, 221.
- 13 F. Geiger, M. Stoldt, H. Schweizer, P. Bäuerle and E. Umbach, Adv. Mater., 1993, 5, 922.
- 14 N. Noma, T. Tsuzuki and Y. Shirota, Adv. Mater., 1995, 7, 647.
- 15 V. Dediu, M. Murgia, F. C. Matacotta, C. Taliani and S. Barbanera, *Solid State Commun.*, 2002, **122**, 181.
- 16 J.-M. Rainmundo, P. Blanchard, H. Brisset, S. Akoudad and J. Roncali, *Chem. Commun.*, 2000, 939.
- 17 M. Turbiez, P. Frere, M. Allain, C. Videlot, J. Ackermann and J. Roncali, *Chem.-Eur. J.*, 2005, **11**, 3742.
- 18 K. Ogawa and S. C. Rasmussen, J. Org. Chem., 2003, 68, 2921.
- 19 S. J. Evenson and S. C. Rasmussen, Org. Lett., 2010, 12, 4054.
- 20 K. R. Radke, K. Ogawa and S. C. Rasmussen, Org. Lett., 2005, 7, 5253.
- 21 H. Mo, K. R. Radke, K. Ogawa, C. L. Heth, B. T. Erpelding and S. C. Rasmussen, *Phys. Chem. Chem. Phys.*, 2010, **12**, 14585.
- 22 (a) M. Parameswaran, G. Balaji, T. M. Jin, C. Vijila, S. Vadukumpully, Z. Furong and S. Valiyaveettil, *Org. Electron.*, 2009, **10**, 1534; (b) G. Balaji, M. Parameswaran, T. M. Jin, C. Vijila, Z. Furong and S. Valiyaveettil, *J. Phys. Chem. C*, 2010, **114**, 4628.
- 23 (a) S. Barlow, S. A. Odom, K. Lancaster, Y. A. Getmanenko, R. Mason, V. Coropceanu, J.-L. Brédas and S. R. Marder, *J. Phys. Chem. B*, 2010, **114**, 14397; (b) L. E. Polander, L. Pandey, S. Barlow, S. P. Tiwari, C. Risko, B. Kippelen, J.-L. Brédas and S. R. Marder, *J. Phys. Chem. C*, 2011, **115**, 23149.
- 24 A. Yassin, P. Leriche and J. Roncali, *Macromol. Rapid Commun.*, 2010, **31**, 1467.
- 25 H.-L. Wong, C.-C. Ko, W. H. Lam, N. Zhu and V. W.-W. Yam, *Chem.-Eur. J.*, 2009, **15**, 10005.
- 26 S. J. Evenson, M. J. Mumm, K. I. Pokhodnya and S. C. Rasmussen, *Macromolecules*, 2011, 44, 835.
- 27 P. Espinet and A. M. Echavarren, Angew. Chem. Int. Ed., 2004, 43, 4704.
- 28 K. Ogawa, Ph.D. Dissertation, North Dakota State University, Fargo, ND, 2005.
- 29 N. Miyaura and A. Suzuki, Chem. Rev., 1995, 95, 2457.
- 30 X. Zhang, J. P. Johnson, J. W. Kampf and A. J. Matzger, *Chem. Mater.*, 2006, **18**, 3470.
- 31 X.-C. Li, H. Sirringhaus, F. Garnier, A. B. Holmes, S. C. Moratti, N. Feeder, W. Clegg, S. J. Teat and R. H. Friend, J. Am. Chem. Soc., 1998, 120, 2206.
- 32 J. Frey, A. D. Bond and A. B. Holmes, Chem. Commun., 2002, 2424.
- 33 T. M. Pappenfus, B. J. Hermanson, T. J. Helland, G. G. W. Lee, S. M. Drew, K. R. Mann, Kari A. McGee and S. C. Rasmussen, *Org. Lett.*, 2008, **10**, 1553.
- 34 A. R. Katritzky and A. F. Pozharskii, *Handbook of Heterocyclic Chemistry*, Pergamon Press, New York, 2nd edn, 2000, p. 61.
- 35 L. Antolini, G. Horowitz, F. Kouki and F. Garnier, *Adv. Mater.*, 1998, **10**, 382.
- 36 J. K. Herrema, J. Wildeman, F. van Bolhuis and G. Hadziioannou, *Synth. Met.*, 1993, **60**, 239.
- 37 (a) R. S. Becker, J. S. de Melo, A. L. Macanita and F. Elisei, *Pure Appl. Chem.*, 1995, **67**, 9; (b) R. S. Becker, J. S. de Melo, A. L. Macanita and F. Elisei, *J. Phys. Chem.*, 1996, **100**, 18683.
- 38 N. R. Krishnaswamy and C. S. S. R. Kumar, *Indian J. Chem., Sect. B: Org. Chem.*, 1993, **32B**, 766.
- 39 (a) T. Benincori, G. Bongiovanni, C. Botta, G. Cerullo, G. Lanzani, A. Mura, L. Rossi, F. Sannicolo and R. Tubino,

- 40 Y. Liu, Y. Sun, Y. Ma, K. Xiao, G. Yu and D. Zhu, Chinese Pat. CN 1,706,848 A, 2005.
- 41 S. Lee, S. Hotta and F. Nakanishi, J. Phys. Chem. A, 2000, 104, 1827-1833
- 42 (a) M. Pasini, S. Destri, C. Botta and W. Porzio, Tetrahedron, 1999, 55, 14985; (b) M. Pasini, S. Destri, C. Botta and W. Porzio, Synth. Met., 2000, 113, 129.
- 43 Y. Sun, Y. Ma, Y. Liu, Y. Lin, Z. Wang, Y. Wang, C. Di, K. Xiao, X. Chen, W. Qiu, B. Zhang, G. Yu, W. Hu and D. Zhu, Adv. Funct. Mater., 2006, 16, 426.
- 44 V. Hernandez, C. Castiglioni, M. Del Zoppo and G. Zerbi, Phys. Rev. B: Condens. Matter, 1994, 50, 9815.
- 45 O. Inganäs, W. R. Salaneck, J. E. Österholm and J. Laakso, Synth. Met., 1988, 22, 395.
- 46 G. Daoust and M. Leclerc, Macromolecules, 1991, 24, 455.
- 47 S.-A. Chen and J.-M. Ni, Macromolecules, 1992, 25, 6081.
- 48 M. Takayanagi, T. Gejo and I. Hanazaki, J. Phys. Chem., 1994, 98, 12893.
- 49 A. R. Katritzky and A. F. Pozharskii, Handbook of Heterocyclic Chemistry, Pergamon, New York, 2nd edn, 2000, pp.70-71.
- 50 B. Xu and S. Holdcroft, Macromolecules, 1993, 26, 4457.
- 51 A. Facchetti, M.-H. Yoon, C. L. Stern, G. R. Hutchison, M. A. Ratner and T. J. Marks, J. Am. Chem. Soc., 2004, 126, 13480.
- 52 I. B. Berlman, J. Phys. Chem., 1970, 74, 3085. 53 M. Belletête, L. Mazerolle, N. Desrosiers, M. Leclerc and G. Durocher, Macromolecules, 1995, 28, 8587.
- 54 N. DiCésare, M. Belletête, A. Donat-Bouillud, M. Leclerc and G. Durocher, J. Lumin., 1999, 81, 111.

- 56 (a) R. J. Waltman and J. Bargon, Can. J. Chem., 1986, 64, 76; (b) S. Ando and M. Ueda, Synth. Met., 2002, 129, 207; (c) C. L. Heth, D. E. Tallman and S. C. Rasmussen, J. Phys. Chem. B, 2010. 114. 5275.
- 57 T. Koopmans, Physica, 1934, 1, 104.
- 58 J. T. Pinhey and E. G. Roche, J. Chem. Soc., Perkin Trans. 1, 1988, 2415
- K. Nozaki, K. Takahashi, K. Nakano, T. Hivama, H.-Z. Tang, 59 M. Fujiki, S. Yamaguchi and K. Tamaoand, Angew. Chem., Int. Ed., 2003, 42, 2051.
- 60 M. J. Frisch, et.al., Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
- 61 A. D. J. Becke, Chem. Phys., 1993, 98, 5648.
- 62 C. T. Lee, W. T. Yang and R. G. Parr, Phys. Rev. B, 1988, 37, 785.
- 63 P. C. Harihara and J. A. Pople, Theor. Chim. Acta, 1973, 28, 213. 64 W. J. Hehre, R. Ditchfield and J. A. Pople, J. Chem. Phys., 1972,
- 56, 2257. 65 M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley,
- M. S. Gordon, D. J. Defrees and J. A. Pople, J. Chem. Phys., 1982, 77, 3654.
- 66 (a) E. Runge and E. K. U. Gross, Phys. Rev. Lett., 1984, 52, 997; (b) E. K. U. Gross and W. Kohn, Adv. Quantum Chem., 1990, 21, 255.
- 67 J. L. Brédas, D. Beljonne, V. Coropceanu and J. Cornil, Chem. Rev., 2004, 104, 4971.
- (a) Standards in Fluorescence Spectrometry, ed. J. N. Miller, Chapman and Hall, New York, 1981, pp. 68-78; (b) Handbook of Organic Photochemistry, ed. J. C. Scaiano, CRC Press, Boca Raton, FL, pp. 233-236.
- 69 R. C. Larson, R. T. Iwamoto and R. N. Adams, Anal. Chim. Acta, 1961, 25, 371.
- 70 C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale and G. C. Bazan, Adv. Mater., 2011, 23, 2367.