

# **CHEMISTRY** A European Journal



WILEY-VCH

# **Accepted Article** Title: Thieno[3,4-c]pyrrole-4,6-dione Oligothiophenes Have Two Crossed Paths for Electron Delocalization Authors: Juan Casado, Dafei Yuan, Samara Medina Rivero, Paula Mayorga Burrezo, Longbin Ren, María E. Sandoval, Sławomir J. Grabowski, David Casanova, and Xiaozhang Zhu This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article. To be cited as: Chem. Eur. J. 10.1002/chem.201801880 Link to VoR: http://dx.doi.org/10.1002/chem.201801880 **Supported by** ACES

# Thieno[3,4-c]pyrrole-4,6-dione Oligothiophenes Have Two Crossed Paths for Electron Delocalization

Dafei Yuan,<sup>[a,c]</sup> Samara Medina Rivero,<sup>[b]</sup> Paula Mayorga Burrezo,<sup>[b]</sup> Longbin Ren,<sup>[a,c]</sup> María E. Sandoval-Salinas, <sup>[d,e]</sup> Sławomir J. Grabowski, <sup>[e]</sup> David Casanova, <sup>[e]</sup> Xiaozhang Zhu,\*<sup>[a,c]</sup> and Juan Casado\*<sup>[b]</sup>

Abstract: We herein report a new series of electron-deficient oligothiophenes, thieno[3,4-c]pyrrole-4,6-dione oligothiophenes (OTPD<sub>n</sub>) from a monomer to a hexamer. We have addressed their optical and structural properties in their neutral states by absorption and emission spectroscopies together with vibrational Raman spectroscopy. In their reduced forms, these molecules can stabilize anions and dianions in similar ways. On the dianions, there are two independent modes of electron conjugation of the charge excess, the interdione path and the interthiophene path, their interference originating the existence of a singlet diradical ground electronic state with the result of the appearance of low energy lying, thermally accessible triplets. Our results provide valuable insights to understand the device performance of TPD-based materials, and for the rational design of new high-performance organic semiconductors.

#### Introduction

During the last decades, thiophene-based  $\pi$ -functional materials have played a crucial role in the development of high-performance organic electronic/optoelectronic devices.<sup>1</sup> Although bare thiophene is electron-rich, it can be transformed into valuable building blocks with widely tunable electron properties by attaching specific substituents (Scheme 1) around the thiophene and in particular in its 3,4 positions (i.e.,  $\beta$  positions) such as poly(3-hexylthiophene-2,5-diyl) (P3HT)<sup>2</sup> and poly(3,4ethylenedioxythiophene) (PEDOT)<sup>3</sup> consisting, respectively, of

[a]	D. Yuan, L. Reng, Prof. X. Zhu
	Beijing National Laboratory for Molecular Sciences, CAS Key
	Laboratory of Organic Solids
	Institute of Chemistry, Chinese Academy of Sciences
	Beijing 100190 (China)
	E-mail: xzzhu@iccas.ac.cn.
[b]	P. Burrezo, S. Rivero, Prof. J. Casado)
	Department of Physical Chemistry
	University of Málaga
	Campus de Teatinos s/n, Málaga, 29071, Spain
	E-mail: casado@uma.es.
[c]	D. Yuan, L. Reng, Prof. X. Zhu
	University of Chinese Academy of Sciences
	Beijing 100190 (China)
[d]	M. E. Sandoval-Salinas
	Departament de Ciència de Materials i Química Física, Institut de
	Química Teòrica i Computational (IQTCUB), Universitat de
	Barcelona
	Martí i Franguès 1-11, Barcelona 08028, Spain.
[e]	M. E. Sandoval-Salinas, S. Grabowski, Prof. D. Casanova
r - 1	Kimika Eagultataa, Euskal Harrika Unibertsitataa (UD)//EHU)

 Kimika Facultatea, Euskal Herriko Unibertsitatea (UPV/EHU), Donostia International Physics Center
 Paseo Manuel de Lardizabal 4, Donostia 20018, Spain

electron-rich 3-hexylthiophene and 3,4-ethylenedioxythiophene, respectively. These are important p-type semiconductors for applications in polymer solar cells as a landmark electron donor material, and these, in some cases, are also widely applied as transparent conductive polymers, such as **PEDOT**:poly(styrenesulfonate).<sup>4</sup> By fusing pro-aromatic benzene, pyrazine, and thiophene rings in the  $\beta$  positions of thiophene, benzo[c]thiophene, thieno[3,4-b]pyrazine and thieno[3,4b]thiophene emerge showing great quinoid-enhancing effect and amphoteric redox behavior, from which homopolymers such as (PIT),5 poly(isothianaphthene) poly(thieno[3,4-b]pyrazine) (PTP),<sup>6</sup> and poly(thieno[3,4-b]thiophene) (PTbT)<sup>7</sup> with relatively small optical bandgaps have been produced (Scheme 1). βfunctionalization with pyrrole diones gives rise to the thieno[3,4c]pyrrole-4,6-dione (TPD) monomer which is a net electronaccepting moiety that produces poly(thieno[3,4-c]pyrrole-4,6dione) (PTPD)<sup>8</sup> with a deep low-energy unoccupied orbitals. Up to date,  $\pi$ -functional materials designed by donor (D)-acceptor-(A) and quinoid strategies have occupied a dominant position in organic photovoltaics,<sup>9</sup> and therefore quinoid-enhancing **TbT** and electron-deficient TPD are highly valuable building blocks in photovoltaic materials.<sup>10,11</sup> **TPD** is clearly an electron-deficient unit which by copolymerizing with weakly electron-rich benzodithiophene (BDT) or thiophene oligomers results in donoracceptor polymers with reduced bandgaps for polymeric solar cells delivering high power conversion efficiencies (PCE) of up to 9.21%.<sup>12</sup> By combining TbT and TPD moieties, we recently developed a new composite acceptor moiety<sup>13</sup> that has been successfully applied for the design of high-performance lowbandgap polymers with PCEs over 9%.14.



**Scheme 1.** Series of Homopolymers Consisting of Thiophene Building Blocks with Dissimilar Electronic Properties.

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The precise understanding of the molecular, electronic and spectroscopic properties of linear oligomers constructed in terms of uniform and continuous enlargement of the number of repeating units is mandatory to understand the properties of analogue polymers and copolymers, or oligomer approach.15 From a fundamental point of view, oligomers provide accurate and unique structure-property relationships which are very beneficial for the knowledge and understanding of the mechanisms of operation and to unravel the design rules for the preparation of new materials with enhanced functionalities.<sup>16</sup> In the context of the oligomer approach, well-defined regioregular oligothiophenes synthesized by efficient "Fibonacci route"17 and EDOT18 and ProDOT oligomers<sup>19</sup> with hexyl side chains and methylthio encapping units were systematically investigated as models of P3HT and PEDOT, as well as oligomers of thieno[3,4b]pyrazine<sup>20</sup> as molecular modes of **PTP**. Furthermore, considering the great success of TbT-based low-band gap polymers, we recently prepared a series of regioregular oligothieno[3,4-b]thiophenes (rr-OTbT)<sup>21</sup> and illustrated the origin of its guinoid-enhancing effect which has helped to successfully develop a series of TbT-based small-molecule optoelectronic materials.22

Although copolymers with **TbT** and **TPD** show high photovoltaic performance, they possess significantly different optical bandgaps, which may be explained by the different "resonance" and "inductive" effect of **TbT** and **TPD** moieties. In order to investigate the nature of **TPD** as an electron-accepting moiety, we present in this article the preparation, structural, and electronic properties of a new series of thieno[3,4-*c*]pyrrole-4,6dione oligothiophenes, **OTPD**<sub>n</sub>, in Scheme 2. Contrarily to the synergistic effect of the **TbT** case, oligomers of **TPD** display a clear opposition between the peripheral dione groups and the central oligothiophene array which establishes two separated electronic domains, among diones and among thiophenes. A complete characterization of the structural, optical, photophysical, redox and spectroscopic properties supported by quantum chemical modeling of the new **OTPD**<sub>n</sub> follows now

#### **Results and Discussion**

#### II. A. Neutral species of OTP<sub>n</sub> oligomers.

**II. A. 1. Synthesis of OTP<sub>n</sub>.** The synthetic route is shown in Scheme 2. Dibromide **Br-TPD-B**r and **Br-OTPD<sub>3</sub>-B**r were synthesized from TPD and **OTPD<sub>3</sub>** with *N*-bromosuccinimide in similar yields of 70%. Similarly, monobromide **TPD-Br**, **OTPD<sub>2</sub>-Br**, and **OTPD<sub>3</sub>-OD-B**r were synthesized with one equivalent *N*-bromosuccinimide. Oligomers with even numbers of repeating units, **OTPD<sub>2</sub>**, **OTPD**<sub>4</sub>, and **OTPD**<sub>6</sub>, were synthesized from Stille-type dimerization of **TPD-Br**, **OTPD<sub>2</sub>-Br**, and **OTPD<sub>3</sub>-Br** in moderate yields of 40%, 30%, and 30% as pale yellow, orange, and red solids, respectively (Scheme 2). The introduction of longer alkyl chain on **OTPD**<sub>6</sub> was to keep the solubility. **OTPD<sub>3</sub>** and **OTPD**<sub>5</sub> with odd numbers of repeating units were obtained by a direct C-H arylation reaction<sup>8</sup> with an excessively ten-equivalent amount of **TPD** as yellow and red solids, respectively. All TPD-

oligomers were fully characterized by conventional methods and the corresponding description is provided in the Supporting Information file (Scheme S1 and Figures S1-S9 for the NMR characterization).



Scheme 2. Synthesis of TPD Oligomers. Reagents and conditions: (a) *trans*bis( $\mu$ -acetato)bis[o-(di-o-tolylphosphino)benzyl]dipalladium(II) (16 mol%), tris(omethyloxy-phenyl)phosphine (60 mol%), potassium acetate (3.0 eq), THF, N<sub>2</sub>, 120 °C, overnight; (b) Sn<sub>2</sub>Me<sub>6</sub> (0.7 eq), Pd(PPh<sub>3</sub>)<sub>4</sub> (8 mol%), dry toluene, N<sub>2</sub>, 110 °C, 2 days.

II. A. 2. Optical and Photophysical Properties. Figure 1 shows the absorption and fluorescence emission spectra of  $OTPD_n$  compounds and Table 1 summarizes the main data.



Figure 1. Top) Absorption and emission spectra at room temperature in CH<sub>2</sub>Cl<sub>2</sub> and their colors in solution (a: OTPD<sub>2</sub>; b: OTPD<sub>3</sub>; c: OTPD<sub>4</sub>; d: OTPD<sub>5</sub>; e: OTPD<sub>6</sub>). Bottom) Representation of the wavelength peak maxima ( $\lambda_{max}$ ) of OTPD<sub>n</sub> as a function of 1/n, with n: number of repeating units (for absorption and emission bands) and for the OT<sub>n</sub> from refs. 23,24. And absorption spectra of OTPD<sub>6</sub> in 2Me-THF on cooling up to 80 K, together with the excitation/emission spectra of OTPD<sub>6</sub> on cooling up to 80 K.

The wavelengths of the peak maxima ( $\lambda_{abs}$ ) of the absorption spectra show a continuous red-shift and color shift from colorless to strongly yellow-orange from the dimer to the hexamer which is similar to that observed in unsubstituted oligothiophenes<sup>23,24</sup> (**OT**<sub>n</sub> in Figure 1 without substitution in the 3,4 positions). The noticeable difference is that, for two oligomers of the same

number of thiophenes, the  $\lambda_{max}$  is more red-shifted in the **OTPD**<sub>n</sub> compounds regarding **OT**<sub>n</sub>. A similar discussion is valid for the emission spectra whose colors now change from strong blue to green also in Figure 1.

Figure 1 also displays the optical properties as a function of the temperature in the case of OTPD<sub>6</sub> in 2-methyl tetrahydrofuran (Figures S10-S11 for the temperature dependent UV-Vis absorption and emission experiments for the rest of samples). At 80 K, the spectrum of OTPD<sub>6</sub> presents three well-defined vibronic peaks (i.e., at 467, 487, and 536 nm) that by increasing the temperature progressively disappear allowing the development of a broad band with a maximum at 440 nm at room temperature. It similarly happens for OTPD<sub>5</sub> and OTPD<sub>4</sub> as a function of the temperature. For OTPD2 and OTPD3 the spectra get also resolved on cooling but with much less noticeable spectral changes. These thermal spectroscopic features have been already observed in unsubstituted oligothiophenes (i.e.,  $OT_n$ ) consisting on room temperature broad and unresolved bands that progressively convert into vibronically resolved features by cooling.<sup>23,24</sup> The distinctive point between  $OT_n$  and  $OTPD_n$  consists in the fact that, for **OTPD**<sub>n</sub>, the resolution of the bands takes place in almost all oligomers whereas in **OT**<sub>n</sub> the vibronic resolution is characteristic long (from hexamers) compounds only.

Table 1. Photophysical and Electrochemical Data of OTPDn.

Property (units)	n=2	n=3	n=4	n=5	n=6
λ <sub>abs</sub> (nm)	362	392	422	438	450
$\epsilon_{\rm max}  (10^5  { m M}^{-1}  { m cm}^{-1})$	0.17	0.20	0.29	0.46	0.64
λ <sub>em</sub> (nm)	419	452	486	510	520
$\Phi^{b}$	8.8	6.8	8.2	11.8	11.8
Stokes shift (eV)	0.47	0.42	0.39	0.40	0.37
<i>E</i> <sub>red</sub> <sup>1/2</sup> <i>c</i> (V)	-1.7	-1.65 -1.85	-1.45 -1.70	-1.40 -1.60	-1.38 -1.55
<i>E</i> <sub>LUMO</sub> <sup>d</sup> (eV)	-3.10	-3.15	3.35	-3.4	-3.42
$E_{g}^{opt}$ (eV)	3.13	2.7	2.53	2.44	2.38

Measured in CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> Absolute fluorescence quantum yield. <sup>c</sup> CV measured in CH<sub>2</sub>Cl<sub>2</sub> (0.1 M Bu<sub>4</sub>NClO<sub>4</sub>, vs Fc/Fc<sup>+</sup>). <sup>d</sup>  $E_{LUMO}$  = -(4.8 +  $E_{red}^{onset}$ ). <sup>e</sup>  $E_{g}^{opt}$  = 1240/ $\lambda_{onset}$  (eV).

The emission spectra of **OTPD**<sub>2</sub> and **OTPD**<sub>3</sub> at room and at low temperature are similar, with well-defined vibronic structures that show mirror-like images regarding the respective excitation spectra (Figures S11). On the other hand, the emission spectra at room temperature of **OTPD**<sub>5</sub> and **OTPD**<sub>6</sub> (see Figure 1 for **OTPD**<sub>6</sub>) are similar to those of **OTPD**<sub>2</sub>/**OTPD**<sub>3</sub>, however, in the frozen solution in **OTPD**<sub>6</sub>, a new emission band at longer wavelengths, at around 650 nm, without fine structure emerges (i.e., this is associated with the same excitation spectrum of that at room temperature). Interestingly, while the wavelength of the highenergy emissions depends on the oligomer length, those at lower energies do not. Figure 1 also compares the chain-length behavior of the wavelength absorption and emission maxima for the **OTPD**<sub>n</sub> oligomers and for the **OT**<sub>n</sub>.<sup>24</sup> Such as mentioned, the absorption wavelength of the broad band (high temperature band) and its associated emission in the **OTPD**<sub>n</sub> display a similar behavior as those of the **OT**<sub>n</sub> with the difference that the wavelengths in the **OTPD**<sub>n</sub> are red-shifted, highlighting the effect of the 3,4-pyrrole-dione substitution on the optical gaps. Conversely, the maxima of the wavelengths of the emissions detected at low energy (> 600 nm) at low temperature display a marked independence with the number of thiophenes.

II. A. 3. Vibrational Raman spectroscopic properties. The Raman spectra of the OTPD<sub>n</sub> compounds at room temperature in Figure 2 show enlightening information. The strongest band at 1533 cm<sup>-1</sup> in OTPD<sub>2</sub>, that downshifts to 1512 cm<sup>-1</sup> in OTPD<sub>6</sub>, is assigned to a collective stretching mode of the successive C=C-C bonds along the oligothiophene spine or bond length alternation modes which undergoes the frequency downshift mentioned above associated with a structural relaxation of the bond length alternation pattern along the  $\pi$ -conjugated path (BLA $\rightarrow$ 0) on  $OTPD_2 \rightarrow OTPD_6$  due to the concomitant increase of  $\pi$ conjugation.<sup>25</sup> However, the stretching band of the carbonyls. v(C=O), at 1755 cm<sup>-1</sup> (see Figure S12 for a spectral zoom in this wavenumber region) is little dependent of the oligothiophene size since they remain far and decoupled of the ground electronic C=C-C conjugation among thiophenes.<sup>26</sup> For OTPD<sub>6</sub>, we have recorded its resonant Raman spectrum, shown in Figure 2 with the 532 nm excitation laser line in the frozen solution. This laser excitation coincides with the vibronic peak at 536 nm and thus provides the vibrational ID of the frozen species (note in Figure 2 that no spectrum at room temperature with the same 532 nm line was recorded). This resonant Raman spectrum shows the disappearance of the 1512 cm<sup>-1</sup> band and the emergence of the v(C=O) bands which are tremendously downshifted up to 1632/1615 cm<sup>-1</sup> in the range of v(C=O) frequencies typical of carbonyls strongly involved in hydrogen bonding.27 This result informs us that on cooling the C=O groups could establish electrostatic interactions with the vicinal sulfur atoms of the thiophenes.23



Figure 2. FT-Raman spectra of OTPD<sub>n</sub> in solid state (a: OTPD<sub>2</sub>; b: OTPD<sub>3</sub>; c: OTPD<sub>4</sub>; d: OTPD<sub>5</sub>; e: OTPD<sub>6</sub>) together with the 532 Raman spectrum of OTPD<sub>6</sub> in 2Me-THF at room temperature and at 90 K (this one is in resonance with the 536 nm band in Figure 1).

Detailed electronic structure characterization by means of natural bond orbital (NBO) analysis (Table S1) indicates the

formation of a O $\rightarrow$ S dative bond in **OTP**<sub>n</sub>. Upon establishing these C=O•••S new non-covalent bonding, the oligothiophenes get much more planar and rigid which would justify (see Scheme 3) the appearance of well resolved vibronic structures for the corresponding absorption bands. In addition, the large involvement of the oxygens in the excited state would impart some  $\pi$ /n character to the low energy lying excitations, thus imparting strong local character and very restricted size dependency such as observed for these >600 nm emissions.



Scheme 3. Interconversion by Means of the Formation/Rupture with Temperature of C=O···S Bonding.

**II. A. 4. Transient Absorption properties: Flash-Photolysis Analysis.** The presence of diones and their participation in the optical properties prompted us to afford the analysis of the pumpprobe absorption spectra with microsecond delay. This is based on the known fact that the presence of carbonyls provides an efficient route for intersystem crossing and, therefore, for the population of triplet excited states. Triplets are excited states with rather large lifetimes, in the regime of microseconds, and consequently microsecond time-resolved transient absorption ( $\mu$ s-TA) is appropriate for their detection.



**Figure 3.** Left: microsecond transient absorption spectra of the  $OTPD_n$  compounds in 2Me-THF at room temperature. (a:  $OTPD_2$ ; b:  $OTPD_3$ ; c:  $OTPD_4$ ; d:  $OTPD_5$ ; e:  $OTPD_6$ ). Right: Fits of the  $\lambda_{max}$  of the TA absorptions of the  $OTPD_n$  compounds and of the  $\lambda_{max}$  of the TA absorption bands of the  $OT_n$  versus 1/n.

Figure 3 displays these  $\mu$ s-TA spectra of the **OTPD**<sub>n</sub> compounds compared with the peak position of the analogue  $\mu$ s-TA spectra for the **OT**<sub>n</sub>.<sup>24</sup> We observe the appearance of a strong triplet-triplet absorption in the 400–600 nm spectroscopic interval upon exciting the broad unresolved absorption band of the **OTPD**<sub>n</sub>. Compared with the spectra of **OT**<sub>n</sub> in Figure 3, we detect a weaker dependence of the  $\lambda_{max}$  of **OTPD**<sub>n</sub> with the enlargement of the molecular size. This reveals again the participation of the dione lateral groups in the electronic excitations of the triplet excited

state manifold, which imparts a smaller dependence of these TA optical properties with the number of thiophenes.

II. A. 5. Electrochemical Properties. The electrochemical properties of the OTPD<sub>n</sub> oligomers have been studied by cyclic voltammetry (CV) in dichloromethane solution at room temperature (Figure 4) and the main data summarized in Table 1. These CVs show the presence in all cases of two cathodic processes corresponding to the consecutive formation of the radical anion and dianion, respectively. Taking OTPD3 as an example, these reductions occur at -1.65 and -1.85 V that pass to -1.45 and -1.70 V in OTPD₄; in the case of OTPD₅ and OTPD6, the two reductions appear at -1.40 and -1.60 V and at -1.38 and -1.55 V, respectively. These data clearly indicate a moderate or small dependence of the reduction potentials with the number of thiophenes, indicative of the stronger involvement of the dione groups. Given that the stabilization of the negative injected charges is driven by the dione groups and considering the symmetry of the molecules, the charge should resonate between pairs of dione groups in such a way that the thiophene also participate but with a secondary role. This is interesting since the injected charge appears as seemingly cross-conjugated with respect to the main inter-thiophene  $\pi$ -conjugated path what would be very relevant in order to describe the nature of the anions and dianions in next sections.



Figure 4. Cyclic voltammetry curves of oligomers  $OTPD_n$  in 0.1 M of Bu<sub>4</sub>NClO<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature (vs Fc/Fc<sup>+</sup>). (a:  $OTPD_1$ ; b:  $OTPD_2$ ; c:  $OTPD_3$ ; d:  $OTPD_4$ ; e:  $OTPD_5$ ; f:  $OTPD_6$ ).

#### II. B. Redox species of the OTP<sub>n</sub> oligomers.

**II. B. 1. Optical properties and unusual structures of the anions and dianions.** The properties of anions and dianions of oligothiophenes have been little (i.e., much less than cations and dications) studied given that oligothiophenes are better suited for the stabilization of cationic species rather than for negative ones.<sup>1,28,29,30</sup> **OTPD**<sup>n</sup> oligomers, therefore, offer a unique opportunity for carrying out a detailed analysis of the optical and

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structural properties of anions and dianions of these particular oligothiophenes owing to the reversibility and stability of these species as deduced from the reversible cyclic voltammetries in section II.5. By using electrochemistry, anions and dianions of the  $OTPD_n$  have been formed and their UV-Vis-NIR and Raman spectra recorded.

The UV-Vis-NIR absorption spectra of the OTPDn are shown in Figure 5 and Figure S13. Reduction of OTPD2 at potentials of the first reversible cathodic wave produces the disappearance of the neutral bands and the rise of only one band at 487 nm (subpeaks at 542/620 nm). On the other hand, by reducing in the first reduction wave of OTPD<sub>3</sub> we detect a main absorption at 552 nm (sub-peaks at 599 nm) and a second broad and weak absorption at 2191 nm; therefore, OTPD<sub>3</sub> follows the typical two bands pattern of the open-shell doublet of anions and cations of linear  $\pi$ conjugated oligomers<sup>30</sup> (these open-shell anion radicals give rise to two excitations involving the doubly occupied, semi-occupied and empty frontier molecular orbitals, or HOMO→SOMO and SOMO  $\rightarrow$  LUMO transitions). For [OTPD<sub>4</sub>]<sup>-</sup>, [OTPD<sub>5</sub>]<sup>-</sup>, and [OTPD<sub>6</sub>]<sup>-</sup>, the two-bands pattern of the absorption spectra is clearly detected at 639/2191 nm, 670/2343 and 688/2416 nm, respectively.

Posterior reduction of the anion radicals provokes the full disappearance of their bands and the progressive growth of new features due to the dianions, ([OTPDn]<sup>2-</sup>). Dianions of linearly  $\pi$ -conjugated molecules are typical closed-shell systems exhibiting a single absorption band in the optical spectra<sup>30</sup> due to the HOMO->LUMO transition. The shape of the absorption spectra of [OTPDn]<sup>2-</sup> do not follow this expected one-band pattern. Indeed, all dianion samples display a two-band pattern very similar to those of the anions.



Figure 5. UV-Vis-NIR absorption spectra of  $OTPD_n,$  obtained electrochemically in a 0.1 M solution of  $Bu_4NPF_6$  in  $CH_2Cl_2$  at room temperature in the cathodic regime.

In particular, the UV-Vis-NIR absorption spectra of  $[OTPD_4]^{2-}$ ,  $[OTPD_5]^{2-}$ , and  $[OTPD_6]^{2-}$  are characterized by two bands blueshifted regarding those of their respective anion radicals at 580/1537 nm, 569/1590 nm and 568/1707 nm, respectively (see Figure 5). This two-band pattern in the absorption spectra of dianions of  $\pi$ -conjugated molecules has been reported in the case of oligofluorenes<sup>31</sup> and assigned to the presence and stabilization of segregated polarons (in the terminology of the authors). Also this is typical of dications of  $\pi$ -conjugated molecules when the dication discloses a polaron-pair structure, which is an open-shell diradical dication in comparison with the most often bipolaron form corresponding to a well-defined closed-shell structure.<sup>32</sup> The separation, or segregation, of the bipolaron structure in two symmetrical polarons (polaron pair) might justify the similitude of the spectra of radical anions and polaron-pair dianions in our **OTPD**<sub>n</sub> compounds.

**II. B. 2. Quantum chemical calculations.** To get further insights on the structure of the dianions of **[OTPD\_n]**<sup>2–</sup>, quantum chemical calculations have been carried out considering their structures either as closed-shell dianions (spin  $\alpha$  and  $\beta$  electrons forced to the same spatial distribution as representative of the bipolaron), or as open-shell dianions (unrestricted Kohn-Sham orbitals), which allow polaron-pair electronic structures (i.e. diradicaloid).

Relative adiabatic energies for the closed-shell and triplet states of  $[OTPD_n]^{2-}$  are represented in Figure 6. The smallest oligomer, i.e.  $[OTPD_2]^{2-}$ , exhibits a closed-shell electronic structure with the triplet state rather high in energy, whereas for the next member,  $[OTPD_3]^{2-}$ , the close-shell configuration is slightly above the open-shell state (~1.15 kcal/mol), meaning that the diradical form becomes more stable. The open- to close-shell gap progressively increases as the number of thiophenes of the oligomer increases. This indicates that the unpaired electrons in the diradical open-shell ground electronic state are electronically coupled and do not appear fully disconnected.



Figure 6. Relative adiabatic energies of the closed-shell (CS) and triplet (T) states with respect to the open-shell configuration at B3LYP/6-31G<sup>\*\*</sup> level for  $[OTPD_n]^{2-}$ .

Assuming a singlet open-shell ground electronic state for  $[OTPD_6]^{2-}$ , TD-DFT excited state calculations have been carried out which nicely predict the appearance of the two-bands pattern such as obtained in the absorption UV-Vis-NIR spectroelectrochemical experiments of  $[OTPD_6]^{2-}$ , the higher energy band at 590 nm (i.e., 568 nm in the experiment) is due to a HOMO-1→LUMO excitation and can be identified as a  $\pi$ - $\pi$ <sup>\*</sup> band between fully occupied and empty orbitals, while the band

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at lowest energy, at 1990 nm (i.e,. 1707 nm in the experiment) arises from an excitation involving the SOMO orbitals, or SOMO $\rightarrow$ LUMO in Figure 7 and, therefore, it can be termed as a polaron-pair band. Computed low-lying excitations for neutral, monoanions and dianions of **OTPD**<sub>n</sub> can be found in Supporting Information (Table S2).



Figure 7. Simulated absorption spectrum for the  $[OTPD_6]^{2-}$  computed at the B3LYP/6-31G\*\* level. Main orbital-to-orbital transitions are shown in the inset.

**II. B. 3. On the diradical character of the dianions.** To further characterize the diradical character of the **[OTPD\_n]**<sup>2–</sup> ground state, we perform restricted active space spin-flip (RAS-SF) calculations.<sup>33</sup> The obtained results (Table 2 and Figure 8) indicate that the **[OTPD\_n]**<sup>2–</sup> oligomers exhibit diradical character for  $n \ge 4$ . For n = 3, the dianion could be labeled as a diradicaloid, while n = 2 holds closed-shell character.



Figure 8. RAS-SF highest occupied natural orbital (HONO) (left) and lowest unoccupied natural orbital (LUNO) (right) for dianions and their electronic occupation numbers.

As a first approximation, the diradical nature can be directly related to the  $\alpha$  and  $\beta$  HOMOs energies and is corroborated by adiabatic S-T energy gaps and by the estimation of the number of unpaired electrons (Table 2 and Figure 8). This confirms that the radical nature comes from the two additional electrons of the dianion and not from the length of the  $\pi$ -conjugation. The length of the oligomer basically controls the interactions between radical

moieties (polarons), but does not provide larger polyradical character (at least up to n = 6). The representation of (RAS-SF) natural orbitals further indicate the diradical character for n > 3 (Figure 8) suggesting the formation of weakly interacting radical moieties located at the two extremes of the oligomer and in line with the formation of segregated or polaron-pair dianions.

Table 2. Singlet-Triplet Energy Gap for [OTPD <sub>n</sub> ] <sup>2-</sup> , n = 2-6. N <sub>U</sub> is the Number of
Unpaired Electrons. (Labels ad and vert in parenthesis indicate the adiabatic
and vertical gaps, respectively. All energies are in kcal/mol.)

			020	
[OTPD <sub>n</sub> ] <sup>2-</sup>	DFT □ <i>E</i> s⊤(ad)	DFT □ <i>E</i> <sub>ST</sub> (vert)	RAS-SF □ <i>E</i> <sub>ST</sub> (vert)	RAS-SF <i>N</i> u
n=2	13.6	21.2	21.3	0.47
n=3	1.5	2.6	1.2	0.86
n=4	0.4	1.0	0.7	1.61
n=5	0.3	0.5	0.5	1.80
n=6	0.4	0.6	0.3	1.84

According to the RAS-SF natural orbitals, each polaron of the pair delocalizes over two vicinal monomers from one carbonyl of the dione in one thiophene to the contiguous which is equivalent to see the dianion as involving two anions, one on each halve of the molecule and that crossed the main interthiophene (through thiophenes) to cover the vicinal diones. Computation of the energy difference between the dianion and twice the monoanion (Figure S14) shows that the interaction between polarons decreases with the number of monomeric units. This energy difference tends to the 1/R decay in the limit of large separation between polarons (n large), that is, it accounts for the repulsion between two negative charges in the long separation, whereas at smaller distances, there is an effective bonding coupling between the SOMO orbitals, which dictates the singlet character of the ground electronic state of the dianion.

II. B. 4. EPR data. Aimed by the small calculated singlet-triplet gaps, we conducted the step-wise reduction titration of OTPD5 by lithium naphthalide up to the anion and dianion and followed the process by electron paramagnetic resonance spectroscopy (Figure 9). As shown in Figure S15, UV-Vis absorption spectra from the chemical reduction are consistent with those obtained electrochemically. The solution color of OTPD₅ changed from yellow (neutral) to light blue (anion, [OTPD5]-), and then pink (dianion, [OTPD5]2-) with increasing amount of lithium naphthalide. As shown in Figure 9, the EPR signal at the field of H = 3384 G for [OTPD5] - confirms its open-shell doublet character. The EPR signal of [OTPD5]2- was also observed which suggests the formation of open-shell diradical dianion. EPR measurements of dianion with increasing temperature are conducted as shown in Figure S16 from 150 K to 298 K observing that the intensity of EPR signal also increased in parallel, which is consistent with the thermal population of the low energy lying triplet predicted for [OTPD<sub>5</sub>]<sup>2-</sup>.

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Figure 9. Color change of the OTPD<sub>5</sub> solution (left) in tetrahydrofuran upon reduction by Li/Naphthalene: yellow (neutral), light blue ([OTPD<sub>5</sub>]<sup>-</sup>), pink ([OTPD<sub>5</sub>]<sup>2-</sup>); EPR spectra of [OTPD<sub>5</sub>]<sup>-</sup> (center) and [OTPD<sub>5</sub>]<sup>2-</sup> (right) at room temperature.

II. B. 5. Raman spectra and structural properties of the negative charged species. For the anions and dianions of the OTPD<sub>n</sub> molecules, resonant Raman spectroscopy has been used to scan the structural properties of the ground electronic states. As a example, Figure 10 shows for OTPD<sub>6</sub> the vibrational Raman spectra taken with the 633 nm laser Raman excitation which enters in full resonance with the absorption bands of both anion and dianion negatively charged species according with the UV-Vis-NIR spectra discussed in section II.B.1 and II.B.2. On one hand, the resonance enhancement of the Raman intensity is appreciated by comparing the solvent bands in the neutral (nonresonant) and in the mono- and dianions species also in Figure 10. Although there are absorbances at 633 nm for the absorptions of the anion with peak maxima at 688/650 nm and of the dianion with peak maximum at 568 nm, by playing with stoichiometric reductions one can safetely obtained the 633 nm resonant Raman spectra of each individual species without mutual interference.



Figure 10. UV-Vis absorption bands of the neutral, anion and dianion of  $OTPD_6$  together with the resonant 633 nm Raman excitation line and 633 nm resonant Raman spectra of the anion and dianion of  $OTPD_6$ .

The relevant and strongest v(C=C) thiophene Raman band of neutral **OTPD**<sub>6</sub> at 1512 cm<sup>-1</sup> moves to 1521 cm<sup>-1</sup> in [**OTPD**<sub>6</sub>]<sup>-</sup> revealing a small affectation of the thiophene vibration if compared with the typical Raman frequency downshifts from the neutral to the radical cation of typical hexathiophenes, of the order of 30–40 cm<sup>-1</sup>.<sup>34</sup> It is also uncommon that upon reduction of the anion to the dianion, the corresponding Raman spectra scarcely change, thus, the spectra of [**OTPD**<sub>6</sub>]<sup>-</sup> and [**OTPD**<sub>6</sub>]<sup>2-</sup> are almost coincident, a similitude of the Raman spectra that should be attributed to the resemblance of their molecular structures. **II. B. 5. A Raman spectra of anions and dianions.** Figure 11 displays the Raman spectra of anions and dianions. Raman spectra for **[OTPD**<sub>4</sub>**]**<sup>-</sup>, **[OTPD**<sub>5</sub>**]**<sup>-</sup> and **[OTPD**<sub>6</sub>**]**<sup>-</sup> could be recorded since they have absorption band at 633 nm excitation, while for the smaller compounds, **[OTPD**<sub>2</sub>**]**<sup>-</sup> and **[OTPD**<sub>3</sub>**]**<sup>-</sup>, the laser excitation does not match resonance with the absorption bands of their anions (see Figure 5).



Figure 11. 633 nm Resonant Raman spectra of the radical anions (left) of  $OTPD_n$  and of the dianions (right) of  $OTPD_n$ . (a:  $OTPD_2$ ; b:  $OTPD_3$ ; c:  $OTPD_4$ ; d:  $OTPD_5$ ; e:  $OTPD_6$ ).

The main Raman bands of these resonant spectra, which emerge from (C=C/C-C) vibrations, are at 1530 cm<sup>-1</sup> for [OTPD<sub>4</sub>]<sup>--</sup> (1524 cm<sup>-1</sup> in neutral), 1523 cm<sup>-1</sup> for **[OTPD<sub>5</sub>]<sup>--</sup>** (1518 cm<sup>-1</sup> in neutral) and at 1521 cm<sup>-1</sup> for **[OTPD<sub>6</sub>]<sup>--</sup>** (1512 cm<sup>-1</sup> in neutral) showing frequency up-sifts regarding those in the neutrals and smaller shifts in the anions in the series (9 cm<sup>-1</sup>, 1530 $\rightarrow$ 1521 cm<sup>-1</sup>) than in the same series of the neutrals (12 cm<sup>-1</sup>, 1524 $\rightarrow$ 1512 cm<sup>-1</sup>). On the other hand, the (C=C/C-C) bands of the Raman spectra of **[OTPD<sub>4</sub>]<sup>2-</sup>**, **[OTPD<sub>5</sub>]<sup>2-</sup>** and **[OTPD<sub>6</sub>]<sup>2-</sup>** are scarcely downshifted with respect to those of the anions in OTPD<sub>5</sub> and unchanged in the case of **OTPD<sub>6</sub>** between its anion radical and dianion.

**II. B. 5. B Theoretical and data and discussion of the Raman spectra.** The similitude and invariance of the spectra of anions and dianions highlights the resemblance of their underlying molecular structures. We have calculated the optimized geometries for the neutral radical anions and dianions. In the case of the latter, these were calculated as open-shell diradical systems (see discussion II.B.2), although it is well known that the geometries calculated at the UB3LYP/6-31G\*\* level for diradical systems are not very accurate, we expect some insight in the evolution of these in comparison with those of the neutral and with the radical anions.

The analysis of the bond length alternation parameter (BLA, average of the difference among the alternating double and single bond distances) in Table 3 from the molecular geometries of the ground electronic state of neutral, radical anions and dianions gives rise to the following information: i) the frequency downshift in the neutral molecules of the  $\Box$ (C=C/C-C) main Raman band of 1524 $\rightarrow$ 1512 cm<sup>-1</sup> in **OTPD**<sub>4</sub> $\rightarrow$ **OTPD**<sub>6</sub> is consistent with the progressive lowering of the BLA in the inter-thiophene (i.e., BLA<sub>IT</sub>) path as 0.055 $\rightarrow$ 0.051 Å in **OTPD**<sub>4</sub>, $\rightarrow$ **OTPD**<sub>6</sub>; ii) The frequency

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upshift of main Raman bands from the neutrals to the anions is consistent with the enlargement of the BLA from that of the interthiophene path (i.e., BLAIT) to those calculated for the interdione paths (i.e., BLA<sub>ID</sub>) such as seen in Table 3; iii) the invariance of the frequencies of the main Raman bands from anions to dianions can be justified by the relatively small changes in the BLA's between the interdione paths, that is from BLA<sub>ID-1</sub> in the anion to BLA<sub>ID-3</sub> in the dianions (Table 3).

Table 3. Bond length alternation (BLA) values (in Å) for the optimized molecular structures of  $\mathbf{OTPD}_n$ ,  $[\mathbf{OTPD}_n]^-$  and  $[\mathbf{OTPD}_n]^{2-}$ , with n = 4-6. BLA<sub>X</sub> (X = IT, ID\_1, ID\_2 and ID\_3) calculated as indicated in insert bellow whith IT = interthiophene, ID = inter-dione.

	BLA ID1	BLA ID_2	BLA ID_3	BLAIT
OTPD₄	0.091	0.094		0.055
[OTPD₄]⁻	0.065	0.049		0.029
[OTPD <sub>4</sub> ] <sup>2-</sup>	0.021	0.070		0.025
OTPD₅	0.091	0.092		0.050
[OTPD₅]⁻	0.073	0.057		0.029
[OTPD <sub>5</sub> ] <sup>2-</sup>	0.027	0.071		0.026
OTPD <sub>6</sub>	0.092	0.094	0.088	0.051
[OTPD <sub>6</sub> ]⁻	0.078	0.065	0.060	0.034
[OTPD <sub>6</sub> ] <sup>2-</sup>	0.038	0.061	0.074	0.025



This discussion of the BLA parameters reveals the existence of two main paths of π-electron delocalization in the charged secies that can be described either in the thienyl chain (interthiophene path or linear  $\pi$ -conjugated path in Figure 12) or delocalized among vicinal diones (interdione path in Figure 12). According to this discussion, the charge is stabilized in the interdione paths in the radical anions affecting the innermost part of the bithiophene segment residing between each pair of dione groups. In the dianion, the two charges occupy very similar bithiophene segments between the interdione paths such as the radical anions, what justifies the UV-Vis-NIR and Raman spectral similitude between monovalent and divalent species. In the dianions, electronic repulsion between the two charges in the interdione paths causes the differences in the absorption spectral wavelengths. Nonetheless, the two embedded radicaloid centers are connected through a sequence of conjugated bonds (see Figure 12 for the antiferromagnetic coupling path) involving the thiophene chain where bonding coupling gives way to the singlet diradical configuration of the ground electronic state and to the low energy lying triplet detected by EPR.



depicting the charge-spin distribution of [OTPD<sub>5</sub>]<sup>2-</sup> as an example. In green, the through-bond antiferromagnetic path. The analogy with TCNE (bottom panel)



Figure 13. Cross-conjugated paths in red designed as 1,2,3 in a) prototypical cross-conjugated triethylene. b) neutral tetracyanoethylene, TCNE, [OTPD<sub>5</sub>]<sup>2−</sup>

The case of [OTPD<sub>n</sub>]<sup>2-</sup> resembles the well-known situation in tetracyanoethylene dianion (TCNE2-) in Figure 13 where the two added charges are stabilized in one dicyanomethylene each with the electronic repulsion leading to a biradical triplet ground electronic state.35 In our cases, the interdione fragment in [OTPD<sub>n</sub>]<sup>2-</sup> compares with the dicyanomethylenes in TCNE<sup>2-</sup>.

However, in TCNE<sup>2-</sup> the path between distal cyanos is not as effective (i.e., ferromagnetic) as the oligothiophene chain (i.e., antiferromagnetic) in **[OTPD\_n]^2**- to mitigate repulsion and for through bond coupling of the two radicals. From another perspective, if the ground electronic state of **[OTPD\_n]^2**- could be described by a linear combination of the three relevant paths,  $\Phi_{IQ}$  (interthiophene quinoidal path),  $\Phi_{ID}$  (interdione path) and  $\Phi_{AF}$  (antiferromagnetic path) in Figure 12, then the total electronic wavefunction is:  $\Phi = a\Phi_{IQ} + b\Phi_{ID} + c\Phi_{AF}$  where *a*, *b* and *c* are the corresponding weigths or contribution coefficients to the total  $\Phi$ , the one of the relevant messages of our work is that *b*>*c*>*a*≠0 for **[OTPD\_n]^2**- indicating that the three play a role, in particular *b* quantifies the total charge stabilization and *c* the through bond radical coupling producing a singlet diradical.

#### Conclusions

In this paper, a new series of well-defined electron-deficient oligothiophenes, OTPD<sub>n</sub>, from the monomer to the hexamer has been prepared serving for the first oligomer approach study of the intensively used TPD building block in organic electronics. We have found the propensity of these molecules for non-bonding C=O····S interactions, which make the molecules to adopt rigid a highly planar structures upon removing thermal disorder. The most outstanding result is the segmentation of the electronic structure of these OTPD<sub>n</sub> provoking the stabilization of dianions as segregated anions or polaron-pair dianions placed in parallel (i.e., in contrast to polaron-pairs in series are described in oligofluorenes). This is the clearest indication of the existence of two paths of  $\pi$ -conjugation: (i) between neighbor diones and (ii) through the thiophene spine. In the neutral state, there are spectroscopic properties associated with the two but upon charging, the electron-deficient character of the diketopyrrol unit accumulates the charge at the interdione  $\pi$ -path which explains the properties of anions and dianions, both similitudes and differences. Whether or not paths (i) and (ii) can be termed as cross-conjugated segments can be qualitatively judged by resonance theory by comparison with the prototypical crossconjugated triethylene<sup>36</sup> such as drawn in Figure 6. In the interdione path canonical form of the dianion, trimethylene moieties are recognized. However, these cross conjugating nuclei do not fully bifurcate the electronic structure but allows inter-spins and through-bond interaction resulting in the existence of a singlet diradical ground electronic state. We here provide valuable insights to rationalize the optoelectronic performance of TPDbased organic materials. This study reveals the rich tunability of oligothiophenes ranging from guinoidal enhanced effect such as in TbT oligomers to segmented  $\pi$ -electronic structures such as in OTPD<sub>n</sub>. Cross conjugation in molecular systems is being revealed as a promising approach for transparent semiconductors<sup>37</sup> and in quantum interference devices.38

## **Experimental Section**

**General Procedure 1:** Preparation of **OTPD**<sub>n</sub>-**Br** (n = 1, 2, 3) and **Br-OTPD**<sub>n</sub>-**Br** (n = 1, 3) from **OTPD**<sub>n</sub>. Compound **OTPD**<sub>n</sub> (1 equiv) was dissolved in CF<sub>3</sub>COOH/ H<sub>2</sub>SO<sub>4</sub> (3/1) under room temperature. *N*-Bromosuccinimide (1 or 3 equiv) was added, and the reactant was stirred overnight. The reaction mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The purification was conducted by using a silica-gel column chromatography with hexane/CH<sub>2</sub>Cl<sub>2</sub> (1:2) as the eluent.

**General Procedure 2:** Preparation of **OTPD**<sub>n</sub> (n = 3, 5) from **Br-OTPD**<sub>n-2</sub>-**Br** and TPD. A mixture of compound **Br-TPD**<sub>n-2</sub>-**Br** (1 equiv), TPD (10 equiv), trans-bis( $\mu$ -acetato)bis[o-(di-o-toylphosphino)benzyl]dipalladium (II) (0.16 equiv), tris(2-methyoxyphenyl)phosphine (0.6 equiv), potassium acetate (3 equiv) in nitrogen-saturated THF (0.25 M) was stirred overnight at 120 °C. After cooling to room temperature, the solvent was removed by evaporation rotary under reduced pressure and the residue was purified by using a silica-gel column chromatography with hexane/CH<sub>2</sub>Cl<sub>2</sub> (1:2) as the eluent.

**General Procedure 3:** Preparation of **OTPD**<sub>n</sub> (n = 2, 4, 6) from **Br-OTPD**<sub>n/2</sub>. Compound **OTPD**<sub>n/2</sub> (1 equiv) were dissolved in dry toluene. Under the N<sub>2</sub> protection, to which Pd(PPh<sub>3</sub>)<sub>4</sub> (0.08 equiv) and Sn<sub>2</sub>Me<sub>6</sub> (0.7 equiv) was added. The solution was stirred under dark at 110 °C for two days. After removal of the solvent, the purification was conducted by using a silica-gel column chromatography with hexane/CH<sub>2</sub>Cl<sub>2</sub> (1:1) as the eluent.

#### 3-Bromo-5,5'-bis(2-ethylhexyl)-4H,4'H-1,1'-bi(thieno[3,4-c]pyrrole)-

**4,4',6,6'(5H,5'H)-tetraone (OTPD<sub>2</sub>-Br).** Pale yellow solid (30%). <sup>1</sup>H NMR (400 MHz, CDCI<sub>3</sub>):  $\delta$  0.89–0.94 (m, 12H), 1.20–1.40 (m, 16H), 1.81 (brs, 2H), 3.56 (m, 4H), 7.89 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCI<sub>3</sub>):  $\delta$  10.4, 14.0, 22.9, 23.0, 23.9, 28.5, 28.6, 30.6, 38.2, 42.7, 42.8, 115.3, 126.7, 132.3, 132.6, 132.8, 134.2, 134.6, 136.7, 161.3, 161.5, 162.0, 162.8. HRMS (MALDI-TOF) calcd for C<sub>28</sub>H<sub>35</sub>BrN<sub>2</sub>O<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 607.129438, found 607.129585. mp: 176 °C.

#### 3-Bromo-5,5',5"-tris(2-octyldodecyl)-4H,4'H,4"H-1,1':3',1"-

ter(thieno[3,4-c]pyrrole)-4,4',4'',6,6',6''(5H,5'H,5''H)-hexaone (OTPD<sub>3</sub>-Br). Yellow solid (30%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.86–0.88 (m, 18H), 1.20–1.50 (m, 96H), 1.88 (brs, 3H), 3.56 (d, 6H), 7.93 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  14.0, 22.6, 26.2, 29.2, 29.3, 29.4, 29.5, 29.6, 29.8, 31.3, 31.8, 36.8, 36.9, 43.0, 43.2, 115.8, 127.0, 131.7, 132.5, 132.9, 133.0, 133.1, 133.6, 133.8, 134.3, 136.9, 161.1, 161.3, 161.8, 162.0, 162.1, 162.4. HRMS (MALDI-TOF) calcd for C<sub>78</sub>H<sub>124</sub>N<sub>3</sub>O<sub>6</sub>S<sub>3</sub>Br [M+Na]<sup>+</sup>: 1396.772785, found 1396.773363. mp: 90 °C.

#### 3,3"-Dibromo-5,5',5"-tris(2-ethylhexyl)-4H,4'H,4"H-1,1':3',1"-

ter(thieno[3,4-c]pyrrole)-4,4',4",6,6',6"(5H,5'H,5"H)-hexaone(Br-OTPD\_3-Br). Yellow solid (70%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.89–0.91(m, 18H), 1.31 (brs, 24H), 1.80–1.86 (m, 3H), 3.57 (d, 6H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ 10.3, 10.4, 14.0, 22.9, 23.0, 23.8, 23.9, 28.4, 28.5, 30.4,30.5, 38.1, 38.2, 42.8, 42.9, 116.1, 132.8, 132.9, 133.3, 134.4, 161.2,161.4, 162.0. HRMS (MALDI–TOF) calcd for C42H51Br2N3O6S3 [M+Na]\*:970.119894, found 970.119869. mp: 220 °C.

#### 5,5'-Bis(2-ethylhexyl)-4H,4'H-1,1'-bi(thieno[3,4-c]pyrrole)-

**4,4',6,6'**(**5H,5'***H***)-tetraone (OTPD<sub>2</sub>).** Pale yellow solid (40%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.87–0.93 (m, 12H), 1.25–1.33 (m, 16H), 1.82 (brs, 2H), 3.56 (d, 4H), 7.88 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  10.4, 14.0, 23.0, 23.8, 28.5, 30.5, 38.2, 42.5, 126.4, 132.5, 133.5, 136.8, 162.3, 162.7. HRMS (MALDI-TOF) calcd for C<sub>28</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 529.218926, found 529.219065. mp: 170 °C.

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#### 5,5',5"-Tris(2-ethylhexyl)-4H,4'H,4"H-1,1':3',1"-ter(thieno[3,4-

**c]pyrrole)-4,4',4'',6,6',6''(5H,5''H)-hexaone (OTPD<sub>3</sub>).** Yellow solid (60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.89–0.95 (m, 18H), 1.29–1.36 (m, 24H), 1.83–1.87 (m, 3H), 3.56 (d, 6H), 7.93 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 10.3, 10.4, 14.0, 23.0, 23.8, 23.9, 28.4, 28.5, 30.4, 30.5, 38.0, 38.2, 42.6, 42.7, 127.0, 132.0, 132.7, 133.5, 133.6, 136.9, 162.0, 162.1, 162.5; HRMS (MALDI–TOF) calcd for C<sub>42</sub>H<sub>53</sub>N<sub>3</sub>O<sub>6</sub>S<sub>3</sub> [M+Na]<sup>+</sup>: 814.298870; found 814.298710. mp: 227 °C.

**5**,**5**',**5**'',**5**'''-Tetrakis(2-ethylhexyl)-4*H*,4'*H*,4''*H*,4'''*H*-1,1':3',1'':3',1'''quater(thieno[3,4-c]pyrrol)-4,4',4'',4''',6,6',6'',6'''(5*H*,5'*H*,5''*H*,5'''*H*)octaone (OTPD<sub>4</sub>). Orange solid (30%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.80–1.0 (m, 24H), 1.32 (brs, 32H), 1.85 (brs, 4H), 3.56 (m, 8H), 7.94 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  10.3, 14.0, 22.9, 23.8, 23.9, 28.4, 28.5, 30.4, 30.5, 38.1, 38.2, 42.6, 42.8, 127.1, 132.1, 132.8, 133.5, 133.7, 134.2, 136.9, 161.9, 162.1, 162.2, 162.5; HRMS (MALDI–TOF) calcd for C<sub>56</sub>H<sub>70</sub>N<sub>4</sub>O<sub>8</sub>S<sub>4</sub> [M+Na]\*: 1077.396870, found 1077.397379. mp: 292 °C.

# 5,5',5'',5'''.Pentakis(2-ethylhexyl)-4H,4'H,4''H,4'''H,4'''H,4'''H,4'''''H,4''''H,4''''H,4''''H,4''''

#### 4,4',4'',4''',4'''',6,6',6'',6''',6''''(5H,5'H,5''H,5'''H,5''''H)-decaone

#### 5,5',5'',5''',5'''',5'''''-Hexakis(2-octyldodecyl)-4H,4'H,4''H,4'''H,4''''H,4''''H,4''''H,1,1':3',1'':3''',1''':3''',1'''':3'''',1''''-

#### sexi(thieno[3,4-c]pyrrole)-

**Computational details:** All geometries have been optimized at the B3LYP level. TDDFT results were done with the same functional. RAS-SF calculations have been performed with 4 electrons in 4 orbitals in the active space. Comparison to other methods can be found as Supporting Information. All calculations have been performed with the 6-31G(d,p) basis set with the Q-Chem packages.<sup>31</sup>

Spectroscopic measurements: UV-Vis absorption spectra were obtained by using a Carv 5000 instrument equipped with a photomultiplier tube R928 and a Cooled PbD Photocell detection system or on a Jasco V-570 . Emission spectra were recorded on a spectrofluorometer from Edinburgh Analytical (FLS920P) equipped with a Xenon lamp and on a Jasco FP-6600 spectrometer. Fluorescent quantum yields (FLQY) were measured on Absolute PL Quantum Yield Spectrometer C11347 from Hamamatsu. All solvent used were of spectroscopic grade purchased from Aldrich. No fluorescent contaminants were detected upon excitation in the wavelength region of experimental interest. For the measurements of the transient absorption spectra in the visible region, a laser flash photolysis system Luzchem LFP-111 was used, with Xe ceramic lamps of 300 W UV-Vis, a 125 mm monocromator, Tektronix TDS 2001C oscilloscope with a bandwidth of 50 MHz and a compact photomultiplier. Samples were excited by third-harmonic generation (355 nm) of a Nd:YAG laser (Lotis TII LS-2132 UTF) controlled by a pulse generator Quantum Composers 9520 with tunable frequencies. FT-Raman spectra were measured using the RAMII FT-Raman module of a VERTEX 70 FT-IR spectrometer. A continuous–wave Nd–YAG laser working at 1064 nm was employed for excitation, at a laser power in the sample not exceeding 30 mW. Raman scattering radiation was collected in a back–scattering configuration with a standard spectral resolution of 4 cm<sup>-1</sup>. 2000 scans were averaged for each spectrum. The Resonant Raman spectra were recorded by using the 633 nm excitation and collected by using the 1 × 1 camera of a Bruker Senterra Raman microscope by averaging spectra during 50 min with a resolution of 3–5 cm–1. A CCD camera operating at –50 °C was used.

**Electrochemical and spectroelectrochemical measures:** Cyclic voltammetry (CV) was performed on a CHI620D potentiostat. All measurements were carried out in a one-compartment cell under an N<sub>2</sub> atmosphere, equipped with a glassy-carbon electrode, a platinum counterelectrode, and an Ag/Ag<sup>+</sup> reference electrode with a scan rate of 100 mV/s. The supporting electrolyte was a 0.1 mol/L dichloromethane solution of tetrabutylammonium perchlorate (TBAP). All potentials were corrected against Fc/Fc<sup>+</sup>. Spectroelectrochemical data were obtained by using an optically transparent thin-layer electrochemical (OTTLE) cell positioned either in the sample compartment of a Cary 5000 Spectrophotometer or of the Raman Senterra spectrometer. The working electrode (Pt minigrid, 32 wires per cm) potential was controlled with an Electrochemical Analyzer BAS 100B and referenced to the Fc/Fc<sup>+</sup> couple.

#### Acknowledgements

We thank the financial support from MINECO, Spain project reference CTQ2015-69391-P. PMB acknowledges financial support from the Juan de la Cierva-Formación 2015 programme supported by MINECO. SMR thanks the ministerio de Economía, Industria y Competitividad of Spain for an FPI grant. This study has been supported by the Basque Government (project IT588-13) and the Spanish Government MINECO/FEDER (project CTQ2016-80955). SJG and DC thank IKERBASQUE, Basque Foundation for Science for financial support. MES acknowledges CONACyT-México for a PhD fellowship (ref. 591700). XZ thank the National Basic Research Program of China (973 Program) (No. 2014CB643502), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB12010200), and the National Natural Science Foundation of China (91333113, 21572234) for financial support.

**Keywords:** thieno[3,4-*c*]pyrrole-4,6-dione • oligothiophene • radical anion dianion • polaron pair • cross conjugation

- I. F. Perepichka, D. F. Perepichka. Handbook of Thiophene-based Materials: Application in Organic Electronics and Photonics, Wiley-VCH, Weiheim, 2009
- [2] T. A. Chen and R. D. Rieke, J. Am. Chem. Soc., 1992, 114, 10087; M. R. Dang, L. Hirsch and G. Wantz, Adv. Mater., 2011, 23, 3597.
- G. Heywang and F. Jonas, *Adv. Mater.* 1992, 4, 116; S. Kirchmeyer and K. Reuter, *J. Mater. Chem.*, 2005, 15, 2077.
- [4] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik and J. R. Reynolds, *Adv. Mater.*, 2000, **12**, 481.
- [5] F. Wudl, M. Kobayashi and A. J. Heeger, J. Org. Chem. 1984, 49, 3382.
- [6] M. Pomerantz, B. Chaloner-Gill, L. O. Harding, J. J. Tseng and W. J. Pomerantz, J. Chem. Soc., Chem. Commun., 1992, 24, 1672.
- [7] M. Pomerantz, X. Gu and S. X. Zhang, *Macromolecules*, 2001, 34, 1817;
   K. Lee and G. A. Sotzing, *Macromolecules*, 2001, 34, 5746.

- [8] P. Berrouard, S. Dufresne, A. Pron, J. Veilleux, and M. Leclerc, J. Org. Chem., 2012, 77, 8167.
- [9] L. Lu, T. Zheng, Q. Wu, A. M. Schneider, D. Zhao and L. Yu, Chem. Rev., 2015, 115, 12666.
- [10] Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, Adv. Mater., 2010, 22, E135.
- [11] Y. Zou, A. Najari, P. Berrouard, Y. Beaupré, Y. Tao and M. Leclerc, J. Am. Chem. Soc., 2010, **132**, 5330; C. Piliego, T. W. Holcombe, J. D. Douglas, C. H. Woo, P. M. Beaujuge and J. M. J. Fréchet, J. Am. Chem. Soc. 2010, **132**, 7595
- [12] J.-H. Kim, J. B. Park, I. H. Jung, A. C. Grimsdale, S. C. Yoon, H. Yang and D.-H. Hwang, *Energy Environ. Sci.*, 2015, 8, 2352.
- [13] C. Zhang, H. Li, J. Wang, Y. Zhang, Y. Qiao, D. Huang, C.-A. Di, X. Zhan, X. Zhu and D. Zhu, *J. Mater. Chem. A*, 2015, **3**, 11194.
- [14] Unpublished results.
- [15] R. Martin and F. Diederich, Angew. Chem., Int. Ed., 1999, 38, 1350.
- [16] J. Gierschner, J. Cornil, H.-J. Egelhaaf, R. E. Martin and F. Diederich, Adv. Mater., 2007, 19, 173.
- [17] F. P. V. Koch, P. Smith and M. Heeney, J. Am. Chem. Soc., 2013, 135, 13695.
- [18] J. J. Apperloo, L.B. Groenendaal, H. Verheyen, M. Jayakannan, R.A.J. Janssen, A. Dkhissi, D. Beljonne, R. Lazzaroni, J.L. Bredas, *Chem.Eur. J.*, 2002, **8**, 2384–2396; M. Turbiez, P. Frere, J. Roncali, *J. Org. Chem.*, 2003, **68**, 5357–5360.
- [19] C. Lin, T. Endo, M. Takase, M. Iyoda and T. Nishinaga, J. Am. Chem. Soc., 2011, **133**, 11339.
- [20] S. C. Rasmussen, R. L. Schwiderski, M. E. Mulholland, *Chem. Comm.*, 2011, **47**, 11394; C. Kitamura, S. Tanaka, Y. Yamashita, *Chem. Mater.*, 1996, **8**, 570–578; J. Casado, R. Ponce Ortiz, M.C. Ruiz Delgado, V. Hernández, J. T, López Navarrete, J.M. Raimundo, P. Blanchard, M. Allain, J. Roncali, *J. Phys.Chem. B*, 2005, **109**, 16616–16627.
- [21] F. Liu, G. L. Espejo, S. Qiu, M. M. Oliva, J. Pina, J. S. Seixas de Melo, J. Casado and X. Zhu, *J. Am. Chem. Soc.*, 2015, **137**, 10357.
- [22] C. Zhang and X. Zhu, Acc. Chem. Soc., 2017, DOI: 10.1021/acs.accounts.7b00050.
- [23] J. J. Apperloo, R. A. J. Janssen, P. R. L. Malenfant and J. M. J. Fréchet, J. Am. Chem. Soc., 2001, 123, 6916; D. Wasserberg, S. C. J. Meskers, R. A. J. Janssen, E. Mena-Osteritz and P. Bäuerle, J. Am. Chem. Soc., 2006, 128, 17007; B. Milián Medina, D. Wasserberg, S. C. J. Meskers, E. Mena-Osteritz, P. Bäuerle and J. Gierschner, J. Phys. Chem. A, 2008, 112, 13282; P. Mayorga Burrezo, B. Pelado, R. Ponce Ortiz, P. De la Cruz, J. T. López Navarrete, F. Langa and J. Casado, Chem. Eur. J., 2015, 21, 1713.
- [24] R. S. Becker, J. S. de Melo, A. L. Maçanita and F. Elisei, J. Phys. Chem., 1996, 100, 18683.
- [25] P. Mayorga Burrezo, J. L. Zafra, J. T. López Navarrete and J. Casado, Angew. Chem. Int. Ed., 2017, 56, 2250.

- [26] R. M. Silverstein, G. C. Bassler and T. C. Morrill, Spectrometric Identification of Organic Compounds.4th Ed., John Wiley and Sons, New York, 1981.
- [27] F. García, P. M. Viruela, E. Matesanz, E. Ortí and L. Sánchez, *Chem. Eur. J.*, 2011, **17**, 7755.
- [28] L. Zhang, N. S. Colella, B. P. Cherniawski, S. C. B. Mannsfeld and A.-L Briseno, ACS Appl. Mater. Interfaces, 2014, 6, 5327; A. Mishra, C.-Q. Ma and P. Baeuerle, Chem Rev., 2009, 109, 1141.
- [29] A. Facchetti, Y. Deng, A. Wang, Y. Koide, H. Sirringhaus, T. J. Marks and R. H. Friend, *Angew. Chem., Int. Ed.*, 2000, **39**, 4547; A. Facchetti, M. Mushrush, H. E. Katz and T. J. Marks, *Adv. Mater.*, 2003, **15**, 33; A. Facchetti, M.-H Yoon, C. L. Stern, H. E. Katz and T. J. Marks, *Angew. Chem., Int. Ed.*, 2003, **42**, 3900.
- [30] J. L. Bredas, J.Chem. Phys., 1985, 82, 3808.
- [31] L. Zaikowski, P. Kaur, C. Gelfond, E. Selvaggio, S. Asaoka, Q. Wu, H. C. Chen, N. Takeda, A. R. Cook, A. Yang, J. Rosanelli and J. R. Miller, J. Am. Chem. Soc., 2012, 134, 10852.
- [32] E. E. Havinga, J. L. van Donger, R. A. J. Janssen, J. Cornil and J.-L. Brédas, *Chem. Eur. J.*, 1998, 4, 1509; S. Rodríguez González, Y. Ie, Y. Aso, J. T. López Navarrete and J. Casado, *J. Am. Chem. Soc.*, 2011, 133, 16350; P. Mayorga Burrezo, J. L. Zafra, J. T. López Navarrete and J. Casado, *Angew. Chem., Int. Ed.*, 2017, 56, 2250.
- [33] D. Casanova and M. Head-Gordon, Phys. Mol. Phys., 2015, 113, 184.
- J. Casado, H. E. Katz, V. Hernandez and J. T. Lopez Navarrete, J.Phys.Chem. B, 2002, 106, 2488; J. Casado, V. Hernandez, S. Hotta and J. T. Lopez Navarrete, J. Chem. Phys., 1998, 109, 10419; J. Casado, V. Hernandez, S. Hotta and J. T. Lopez Navarrete, Adv. Mater., 1998, 10, 1258; J. Casado, L. L. Miller, K. R. Mann, T. M. Pappenfus, Y. Kanemitsu, E. Orti, P. M. Viruela, P. Pou-Amerigo, V. Hernandez and J. T. Lopez Navarrete, J. Phys. Chem. B, 2002, 106, 3872; J. Casado, L. L. Miller, K. R. Mann, T. M. Pappenfus, V. Hernandez and J. T. Lopez Navarrete, J. Phys. Chem. B, 2002, 106, 3597.
- [35] J. S. Miller, Angew. Chem., Int. Ed. 2006, 45, 2508–2525; Angew. Chem. 2006, 117, 2570–2588.
- [36] N. F. Phelan, M. Orchin, *J. Chem. Educ.*, **1968**, *45*, 633; A. D. Payne, G. Bojase, M. N. Paddon-Row, M. S. Sherburn, *Angew. Chem. Int. Ed.*, **2009**, *48*, 4836.
- [37] X. Qiao, Q. Wu, H. Wu, J. Zhang and H. Li, *Adv. Funct. Mater.*, 2017, 27, 1604286; B. Xia, K. Lu, Y. Zhao, J. Zhang, L. Yuan, L. Zhu, Y. Yi and Z. Wei, *Adv. Sci.*, 2015, 2, 1500021.
- Y. Tsujia , R. Hoffmanna, M. Strangeb , G. C. Solomon, *PNAS*, 2015, 113, E413–E419; C. J. Lambert, *Chem. Soc. Rev.*, 2015, 44, 875–888.
   M. L. Kirk, D. A. Shultz, D. E. Stasiw, D. Habel-Rodriguez, B. Stein, P. D. Boyle, *J. Am. Chem. Soc.* 2013, *135*, 14713–14725.

# **FULL PAPER**

## **Entry for the Table of Contents**

# FULL PAPER



Electron-deficient thieno[3,4-*c*]pyrrole-4,6-dione oligothiophenes show two distinctive path for p-electron delocalization in their neutral state and as a result are able to singularly stabilize radical anions and dianions in a different way as unsubstituted oligothiophenes do. These two cross-conjugated paths are: (i) between neighbor diones and (ii) through the thiophene spine. Cross-conjugated molecules promise important future applications as  $\pi$ -functional materials.

D. Yuan, S. Rivero, P. Burrezo, L. Ren, M. Sandoval-Salinas, S. Grabowski, D. Casanova, X. Zhu,\* and J. Casado\*

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Thieno[3,4-*c*]pyrrole-4,6-dione Oligothiophenes Have Two Crossed Paths for  $\pi$ -Electron Delocalization