# Journal of Materials Chemistry C

# PAPER



View Article Online View Journal | View Issue

Cite this: J. Mater. Chem. C, 2014, 2, 4276

Received 4th March 2014 Accepted 1st April 2014

DOI: 10.1039/c4tc00427b

www.rsc.org/MaterialsC

## Introduction

The search for new materials that can be used in optoelectronic applications such as organic photovoltaics (OPVs),<sup>1</sup> organic light-emitting field-effect transistors (LEFETs),<sup>2</sup> or organic lightemitting diodes (OLEDs)<sup>3</sup> has been, and remains an important challenge. Indeed, new materials (small molecules, dendrimers or polymers) with tailored optical and electronic properties are needed to better understand the interplay between molecular and film structure, and charge-transport and optical properties. Understanding these structure–property relationships will ultimately lead to the development and optimisation of new materials. Thus, it is important to identify the key building blocks for each application. In the field of OPV one approach to select building blocks has been to choose deeply coloured

# Synthesis and properties of pyrrolo[3,2-b]pyrrole-1,4-diones (isoDPP) derivatives<sup>†</sup>

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The synthesis of three pyrrolo[3,2-b]pyrrole-1,4-dione (isoDPP) derivatives is described, namely 1,3,4,6tetraphenylpyrrolo[3,2-b]pyrrole-2,5(1H,4H)-dione **2**, 1,4-diphenyl-3,6-di(thiophen-2-yl)pyrrolo[3,2-b]pyrrole-2,5(1H,4H)-dione **3**, and 1,4-bis(4-(hexyloxy)phenyl)-3,6-di(thiophen-2-yl)pyrrolo[3,2-b]pyrrole-2,5(1H,4H)-dione **7** in which the molecular structures differ in the aromatic ring (phenyl or thiophene) attached to the nitrogen atom. Thin films of **2**, **3**, and **7** could be formed by evaporation under vacuum. In the case of **2** and **3** GIWAXS measurements showed that the film structural ordering was similar to that measured in single crystals. In contrast GIWAXS showed that **7** had features associated with liquid crystalline materials. Time dependent density functional theory (TDDFT) calculations predicted that the transition between the lowest energy singlet excitation (S<sub>1</sub>) and the ground state (S<sub>0</sub>) would be optically forbidden due to the centrosymmetric geometries of compounds. Photophysical measurements showed that the compounds were weakly luminescent, with low radiative rates in solution of order 10<sup>6</sup> s<sup>-1</sup>, which are consistent with the TDDFT predictions. Furthermore, photoinduced absorption (PIA) spectroscopy showed that there is a long-lived low energy state, which has been assigned as a triplet and provides a further non-radiative decay pathway for the excited state.

organics dyes or high electron affinity moieties as a mean to control the properties, and in particular when used with units of low ionisation potential, to shift the absorption to longer wavelengths. In recent times, several building blocks have been investigated, including diketopyrrolopyrroles (DPP),<sup>4</sup> iso-indigo,<sup>5</sup> thienopyrroledione (TPD),<sup>6</sup> benzothiadiazole (BT),<sup>7</sup> and thienothiophene,<sup>8</sup> leading to materials that have good performance in a range of devices.

Currently pyrrolo[3,4-c]pyrrole-1,4-dione (DPP) is one of the most popular units used in the preparation of non-polymeric (often erroneously termed "small molecules") and polymeric materials for optoelectronic applications. In fact, the DPP unit was first reported by Farnum in 1974 as an undesired side product.9 Since then, the optical, thermal, physical and electronic properties have been studied extensively in a plethora of derivatives. For instance, excellent charge transporting properties (hole and electron mobilities of 10.5 and 3 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively),10 and/or high PCEs (up to 6.5%) in photovoltaic devices11 have been observed when the DPP moiety is used as a component within conjugated copolymers. In contrast, the regioisomeric pyrrolo[3,2-b]pyrrole-1,4-dione (isoDPP) unit has not attracted much attention (Fig. 1). The synthesis was described by Langer et al.,<sup>12</sup> but it is only recently that it has been used as a monomer unit in conjugated polymers. The small number of isoDPP-based copolymers that have been used in OPVs or OFETs devices have shown promising results in

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<sup>†</sup> Electronic supplementary information (ESI) available. CCDC 975864–975866. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4tc00427b



Fig. 1 Molecular structures of pyrrolo[3,4-c]pyrrole-1,4-dione (DPP) and pyrrolo[3,2-b]pyrrole-1,4-dione (isoDPP).

terms of device performance.<sup>13</sup> However, the fundamental solid state properties of the simple isoDPP unit have yet to be explored in detail.

In this work we have used a systematic approach to study the effect molecular packing has on the thermal and the optical properties of three isoDPP model compounds. We have varied the chemical structure by changing the aromatic groups (phenyl to thiophene) and by adding alkoxy chains to enhance the solubility. We have measured the single-crystal and thin-film structures for the compounds and have investigated the photophysical properties by steady-state and time-resolved spectroscopic methods.

### Results and discussion

The synthetic pathways to compounds 2, 3 and 7 are illustrated in Scheme 1. The first step in the syntheses of 2 and 3 was the preparation of the oxanilide by the addition of oxalyl chloride to aniline in toluene.14 After a few minutes, a slurry was obtained, which was then directly chlorinated with phosphorous pentachloride to give the bis-phenylimidoyl chloride 1. We found that intermediate 1 was not stable under ambient conditions and must be quickly used in the next step without purification. Reaction of 1 with the enolate of ethyl-2-phenylacetate (formed by deprotonation with lithium di-iso-propylamide) gave compound 2 in a moderate yield of 54%. Following the same procedure as before, but using the enolate of ethyl-2-(thiophen-2-yl)acetate, resulted in the formation of compound 3 in a yield of 39%. Given the poor solubility of 2 and 3 we decided to prepare a derivative that had *n*-hexyloxy substituents on the *N*phenyl ring. To do so, we synthesised the corresponding aniline 4 following a literature procedure,<sup>15</sup> and then reacted this with oxalyl chloride to give 5, phosphorous pentachloride to form 6, and finally ethyl-2-(thiophen-2-yl)acetate to generate compound 7 in a yield of 36%. Compounds 2 and 3 have low solubility in common organic solvents such as dichloromethane and tetrahydrofuran, although they showed better solubility in boiling N,N-dimethylformamide and 1,2-dichlorobenzene. In contrast, compound 7 was found to be soluble in a range of organic solvents, as expected from the addition of an alkoxy chain onto each of the two phenyl rings.

To understand the solid state molecular ordering and packing of these materials, single crystals were grown. Single crystals for compounds **2** and **3** were successfully grown from *N*,*N*-dimethylformamide whereas crystals of **7** were obtained using an interface diffusion method, employing dichloromethane as the good solvent and *n*-hexane as the non-solvent. Table 1 summarizes the crystallographic data of these three compounds, and Fig. 2 shows their molecular packing. As shown in Table 1, we note that all three isoDPP derivatives have the same monoclinic crystal system. Moreover, compounds 2 and 3 have the same  $P2_1/n$  space group, whereas compound 7 has the standard  $P2_1/c$  space group.

From the crystal structures we see that the dihedral angles of the two linkages,  $\varphi$ N and  $\varphi$ C, of 2, 3, and 7 (see table in Fig. 3) are relatively large meaning that the attached phenyl and thiophene rings are not in the same plane as the isoDPP unit. The phenyl rings linked to the nitrogen atom have very similar  $\varphi N$ values (64-70°) for the three compounds. Substituting the phenyl with a thiophene ring does lead to a reduced dihedral angle at the carbon ( $\varphi$ C from 36.5° for 2, to 24.7° and 21.2° for 3 and 7, respectively) although  $\varphi$ N stays the same. In other words the phenyl rings linked on the nitrogen atoms are the dominant factor in controlling the structure and  $\pi$ - $\pi$  intermolecular interactions. In contrast, when aromatic groups are attached to the DPP moiety they lie in the same plane. In considering the interchromophore distances the crystal structures show two different spacings. If the isoDPP only was considered it can be seen that for compounds 2 and 3 the inter-planar distances (from ketone oxygen to ketone oxygen) are 5.2 Å and 4.2 Å, respectively (see Fig. 3). Replacing a phenyl ring by a thiophene ring reduces the inter-plane distance in the case of compound 3. In the case of 7 the addition of an alkyloxy chain onto the phenyl ring leads to additional disruption to the close packing of the isoDPP units, as shown in Fig. 2(e). For compound 7, it can be clearly seen that in the unit cell the two alkyloxy chains are intercalated between the isoDPP molecules within the same plane of the unit cell. We also note that the bond angle between the CH<sub>2</sub> and -CH<sub>3</sub> on the alkyl chain is 90°. This unexpected behaviour has also been reported for another isoDPP derivative,16 and as a consequence the inter-plane distance for 7 was much larger (10.7 Å) than that measured for 2 and 3 (Fig. 3). However, for these three compounds the closest  $\pi$ - $\pi$  interactions are between the side groups. In the case of compounds 2 and 3 the closest  $\pi$ - $\pi$  interactions are between the phenyl rings attached to the nitrogens with distances of around 3.5 Å and 3.7 Å, respectively. In contrast, in the case of 7 the nearest interactions are between the phenyl and thiophene units on adjacent chromophores ( $\approx$  3.6 Å).

To determine whether the crystal structure mapped onto the thin film structure we carried out grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements on vacuum evaporated non-annealed films.<sup>17</sup> Fig. 4 presents the 2D GIWAXS patterns of the vacuum evaporated films. For the case of compounds 2 and 3 the corresponding GIWAXS patterns show clear crystalline peaks indicative of a highly crystalline microstructure. In contrast, the GIWAXS pattern of compound 7 shows no crystalline peaks indicating a less ordered thin film structure. For the film of compound 2, all the observed GIWAXS peaks except for the peak at  $0.6 \text{ Å}^{-1}$  can be indexed to the single crystal structure reported above [see Fig. 4(a)] with the relative intensities of the observed peaks also matching that predicted

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Scheme 1 Conditions and reagents (i) oxalyl chloride, then PCl<sub>5</sub>, toluene,  $\Delta$ . (ii) LDA, ethyl-2-phenylacetate 1 h, THF, (acetone/dry ice bath) then 1 was added (acetone/dry ice bath) then 14 h, r.t. (iii) LDA, ethyl-2-(thiophen-2-yl)acetate 1 h, THF, (acetone/dry ice bath) then 1 was added (acetone/dry ice bath) then 14 h, r.t. (iv) Oxalyl chloride, Et<sub>3</sub>N, THF, 2 h. (v) PCl<sub>5</sub>, toluene, 2 h,  $\Delta$ . (vi) LDA, ethyl-2-(thiophen-2-yl)acetate 1 h, THF, (acetone/dry ice bath) then 6 was added (acetone/dry ice bath) then 16 h, r.t.

Table 1 Crystallographic data for compounds 2, 3, and 7

Crystal	2	3	7
Empirical formula	$C_{30}H_{20}N_2O_2$	$C_{26}H_{16}N_2O_2S_2$	$C_{38}H_{40}N_2O_2S_2$
Molecular weight $(g \text{ mol}^{-1})$	440.46	452.55	652.87
Crystal habit, color	Needle, orange	Needle, red	Needle, light red
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_{1}/c$
a (Å)	6.2448(16)	12.2888(14)	5.7794(4)
b (Å)	11.883(3)	5.8588(5)	13.9768(9)
<i>c</i> (Å)	14.808(5)	14.7622(15)	20.7994(11)
α (°)	90.00	90.00	90.00
$\beta$ (°)	100.99(3)	107.799(11)	96.686(6)
$\gamma$ (°)	90.00	90.00	90.00
$V(Å^3)$	1078.7	1011.97	1668.7
Z	2	2	2
R Factor (%)	5.68	3.44	4.21
Density (g cm $^{-3}$ )	1.356	1.485	1.299

by the single crystal structure. The scattering observed in Fig. 4(a) for compound 2 is also anisotropic indicating a preferred orientation of the molecules relative to the substrate.

In particular the 002 peak is found to be oriented along  $q_z$ indicating that this crystallographic axis is highly oriented outof-plane (directed along the surface normal). Such an orientation corresponds to an orientation of the unit cell such that the normal of the isoDPP cores are oriented approximately 40 degrees from surface normal, as shown schematically in Fig. 4(b). The unexplained peak at  $q = 0.6 \text{ Å}^{-1}$  indicates the presence of a minority population of molecules that exist in a second, unknown crystal structure. Similar to compound 2, the scattering peaks observed for compound 3 are found to match those expected based on the single crystal structure of compound 3. Unlike compound 2, all the peaks observed in the GIWAXS pattern of compound 3 can be attributed to reflections expected from the single crystal structure indicating only one crystalline form. The GIWAXS pattern of compound 3 has the 100 axis oriented largely out of plane with the 010 axis at  $\approx$  30 degrees from the surface normal, indicating an orientation schematically depicted in Fig. 4(d). In this orientation, the normal of the isoDPP cores are oriented approximately 70 degrees from surface normal. In both of these thin films, the isoDPP cores, although tilted very differently, stack in columns parallel to the substrate. The GIWAXS peaks for compound 3 are



Fig. 2 Molecular packing observed in single crystals for (a) compound 2 unit cell viewed along a axis, (b) compound 2 unit cell viewed along b axis, (c) compound 3 unit cell viewed from a axis, (d) compound 3 unit cell viewed along b axis, (e) compound 7 unit cell viewed from a axis, (f) compound 7 unit cell viewed along c axis. Atoms of C, O, N and S are shown in gray, red, magenta, and yellow, respectively.



Compound	InterplaneNearest $\pi$ - $\pi$ isoDPP distancedistance		$arphi \mathrm{N}^{\mathrm{b})}$	$\varphi C^{c)}$
	Å	Å	(°)	(°)
2	5.2	3.5	-63.5	36.5
3	4.2	3.7	-67.5	24.7
7	11.7	3.6	-70.1	21.2

<sup>a)</sup> The interplane distance was calculated from the shortest oxygen atom distance (ketone to ketone) on adjacent units. <sup>b)</sup> Nitrogen-phenyl dihedral angles ( $\phi$ N) obtained from single-crystal structures. <sup>c)</sup> Carbon-phenyl/thiophene dihedral angles ( $\phi$ C) obtained from single-crystal structures.

Fig. 3 Interplanar distance (a) and dihedral angles (b and c) for compounds 2, 3 and 7.



Fig. 4 Thin film results (a) 2D GIWAXS pattern of compound 2, (b) schematic of crystal structure of compound 2 in a thin film, (c) 2D GIWAXS pattern of compound 3, (d) schematic of crystal structure of compound 3 in a thin film (e) 2D GIWAXS pattern of compound 7.

significantly more arced than compound 2 indicating increased orientational disorder with the 100 axis of crystallites adopting a broad range of orientations about the surface normal. From the GIWAXS pattern of compound 7 [Fig. 4(e)] there is no evidence that the single crystal structure is adopted in the thin film. There is some structure in the GIWAXS pattern indicating very short range correlations. Evidence for slightly longer range order (albeit only over  $\approx$ 7 repeat units) is found in the peaks at  $q \approx 1.6$  Å<sup>-1</sup> corresponding to a spacing of 3.9 Å consistent with  $\pi$ - $\pi$  stacking. This apparent  $\pi$ - $\pi$  stacking peak is observed for two orientations, one normal to the substrate and one at approximately 45 degrees from normal possibly indicating two populations. Despite the non-crystalline nature of the film there is orientational order throughout the film similar to that of a nematic phase liquid crystal.

To complete the physical characterisation of the three isoDPP derivatives, we investigated their thermal properties. The melting points of the compounds were relatively high (>300 °C for compounds 2 and 3, and 250 °C for compound 7), which are similar to those reported for DPP-based molecules.<sup>18</sup>

The thermal stability of the three compounds was obtained using Thermal Gravimetric Analysis (TGA), with the samples being heated at a rate of 10 °C min<sup>-1</sup> under nitrogen (Fig. 5). Compounds 2 and 3 were found to have  $T_d = 327$  °C and 350 °C, respectively ( $T_d$  is the temperature at which a 5% weight loss was observed). Hence, substituting the phenyls with thiophene rings had only a small effect on the melting or the degradation temperatures. Although the addition of the alkyl chain on the phenyl ring lowered the melting point (compound 7), the thermal stability remained high ( $T_d = 383$  °C). Differential scanning calorimetry showed that the compounds did not have glass transitions in the temperature range of 0 °C to 190 °C (see ESI†).

In the next step of the study we measured the ionization potential (IP) of the compounds using photoelectron spectroscopy in the air (PESA) and the results are reported in Table 2. We found that the ionization potentials of compounds 3 and 7, bearing thiophene rings, range from -5.88 to -5.73 eV respectively. For compound 2 the ionization potential was outside the limits of the instrument response and hence is greater than -6.2 eV. It is clear that with such large ionisation potentials it would be difficult to achieve ohmic contacts for hole injection with these simple isoDPPs. The relatively large ionisation potential of a similar compound to 7 could not be measured electrochemically due it falling outside the solvent window.<sup>19</sup>

Density functional theory (DFT) calculations were undertaken in order to investigate and compare the electronic structures of the compounds. Details of the results obtained from the DFT calculations are shown in Fig. 6 and 7, and tabulated in the ESI.† At this level of analysis a number of important similarities between the compounds are observed. First, there are three key frontier orbitals in each of the compounds: the lowest unoccupied molecular orbital (LUMO), highest occupied molecular orbital (HOMO) and the HOMO–1. (In compound 7 the HOMO–2 and HOMO–3 are also important for a full understanding of the excitation spectrum as we will discuss below, *cf.*, Fig. 7.) The HOMO–1 is important in all three compounds



Fig. 5 TGA thermograms of compounds 2, 3 and 7.

Table 2 Optical and electronic properties of compounds 2, 3, and 7

$\lambda_{\max}$		$\lambda_{em}$			
Soln, <sup>a</sup> nm	Film, nm	Soln, <sup>a</sup> nm	Film, nm	IP, <sup>b</sup> eV	
348	373	631	645	>-6.20	
412	420	653	675	-5.88	
412	415	713	698	-5.73	
	λ <sub>max</sub> Soln, <sup><i>a</i></sup> nm 348 412 412	$\lambda_{\max}$ Soln, <sup><i>a</i></sup> nm Film, nm 348 373 412 420 412 415	$ \frac{\lambda_{\max}}{\text{Soln},^{a} \text{nm}}  Film, \text{nm}}  \frac{\lambda_{em}}{\text{Soln},^{a} \text{nm}} $ 348 373 631 412 420 653 412 415 713	$\begin{array}{c c} \lambda_{\max} & \lambda_{em} \\ \hline Soln,^{a} nm & Film, nm & Soln,^{a} nm & Film, nm \\ \hline 348 & 373 & 631 & 645 \\ 412 & 420 & 653 & 675 \\ 412 & 415 & 713 & 698 \\ \hline \end{array}$	

<sup>*a*</sup> In dichloromethane. <sup>*b*</sup> From photoelectron spectroscopy in the air (PESA).



Fig. 6 Calculated frontier molecular orbital energies and Kohn–Sham orbitals for compounds 2, 3 and 7 from DFT (ADF; B3LYP/TZP). All orbitals are labelled as even (A<sub>g</sub>) or odd (A<sub>u</sub>) with respect to inversion.† In parenthesis: IP from PESA measurements (see Table 2).



Fig. 7 Calculated energies of the four highest energy occupied Kohn–Sham molecular orbital for compounds 2, 3 and 7 from DFT (ADF; B3LYP/TZP). All orbitals are labelled as even  $(A_g)$  or odd  $(A_u)$  with respect to inversion.

because the HOMO and HOMO-1 have only a small energetic separation relative to the HOMO-LUMO gap [and indeed the typical molecular orbital (MO) gaps in these compounds]. This

already suggests that the excited states of these compounds will be more complex than the normal consideration of the simple HOMO-LUMO energy gap.<sup>20</sup> Turning to analyse the electron distributions of the molecular orbitals (MOs) it can be seen that the LUMO is primarily localized on the isoDPP core, independent of the substituents on the nitrogen and carbon atoms. It can also be seen that for 2 there is LUMO density on the phenyl side groups attached to the carbon atoms and this is replicated for the attached thiophene rings for 3 and 7. In contrast, the HOMO and HOMO-1 density is more evenly distributed over the groups of each of the molecules independent on whether the ring is a phenyl or thiophene, or indeed attached to a carbon or nitrogen of the isoDPP unit. The calculated energy levels for the HOMOs were found to follow the experimentally determined trend in the IP (see Fig. 6 and Table 2).

To understand the nature of the excited states we performed time-dependent DFT (TDDFT) calculations for 2, 3 and 7. The calculated excitation spectra are reported in Fig. 8 and the energies, oscillator strengths and characters of the ten lowest singlet and triplet excitations are tabulated in the ESI.<sup>†</sup> In order to understand these results it is helpful to note that all three compounds are centrosymmetric, *i.e.*, symmetric under inversion, which maps the spatial coordinates  $(x, y, z) \rightarrow (-x, -y, -y, z)$ -z; all three molecules have  $C_i$  symmetry. Thus all of the orbitals must be either even or odd under inversion; labelled Ag and Au respectively. In all three molecules the LUMO is Au. In 2 and 7 the HOMO is  $A_u$  and the HOMO-1 is  $A_g$ , whereas these levels cross in 3 meaning that the HOMO is Au and the HOMO-1 is Ag. In 2 and 3 the two lowest lying singlet excitations, which are predominately HOMO  $\rightarrow$  LUMO and HOMO-1  $\rightarrow$  LUMO (see ESI<sup>†</sup> for details), are either A<sub>g</sub> (A<sub>u</sub>  $\rightarrow$  A<sub>u</sub>) or A<sub>u</sub>  $(A_g \rightarrow A_u)$ . However, for 2 and 3 the HOMO and HOMO-1 are sufficiently close in energy that the relative energies of the many-body states is determined by the degree of mixing with higher lying molecular orbital transitions more than the relative energies of the HOMO and HOMO-1. Thus, in 2 and 3  $S_1$  is  $A_g$ and S<sub>2</sub> is A<sub>u</sub>. As the electric dipole is antisymmetric (A<sub>u</sub>) under inversion Ag transitions are dipole forbidden. Therefore the TDDFT calculations predict that S1 is dark and S2 is the lowest energy emissive excitation in 2 and 3. We expect this to have clear signatures in the photophysical properties of these molecules.

In 7 the excitation spectra is somewhat more complicated. This can be understood by comparing the DFT and TDDFT results. Firstly, from the results plotted in Fig. 7, it is clear that the HOMO–HOMO–1 gap is substantially larger in 7 than in either 2 or 3. Furthermore, the HOMO–2 and HOMO–3 are much closer (in energy) to the HOMO for 7 than they are in either 2 or 3. This has important consequences for the TDDFT excitation spectra. Note that the LUMO+1 (and higher lying virtual levels; *cf.* ESI†) remain at significantly higher energies ( $\sim$ 2 eV) than the LUMO in all three compounds and therefore play only minor roles in the low-energy excited states. In 2 and 3 the low-energy singlet excitations are quite pure inter-MO transitions due to the relatively large energy separations and symmetry constraints. But, for 7, there is strong mixing of the MO transitions, consistent with the small energy gaps. In all

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Fig. 8 (a-c) Calculated excitation spectra. The symmetry of the excitations are colour coded as indicated in the key. (d-f) Oscillator strengths of the transitions. As the Ag and triplet transitions are optically forbidden their locations are marked by a cross.

three compounds the brightest transition is dominated by the transition from the highest energy  $A_g$  MO to the  $(A_u)$  LUMO. In 2 and 3 this is  $S_2$ , which is 86% HOMO-1  $\rightarrow$  LUMO in 2 and 96% HOMO  $\rightarrow$  LUMO in 3. But, in 7 the strong mixing means that this is  $S_5$ , which is HOMO-1  $\rightarrow$  LUMO (52%), HOMO-2  $\rightarrow$  LUMO (29%), and HOMO-4  $\rightarrow$  LUMO (15%), *i.e.*, highly mixed. An important consequence of this mixing is to push the brightest excitation to relatively higher energy in 7 (compared with 2 and 3).

Therefore, with a clear theoretical framework for the optical transitions the final aspect of this study was an investigation of the photophysical properties of the materials. The absorbance and photoluminescence spectra of compounds 2, 3 and 7 in solution and the solid-state are shown in Fig. 9, with the results summarised in Table 2. In solution all compounds show a broad absorption peak with a weak absorption tail at longer wavelengths. In previous work the low energy absorption feature was assigned to the transition of lowest lying singlet

excited state, which had a weak oscillator strength,<sup>19</sup> and this is consistent with our calculations. In solution compound 2 had an absorption peak at 353 nm while compounds 3 and 7, which contain the thiophene rings, had maxima at 415 nm. In moving to the solid state the peak maximum for 2 moved to 373 nm, whereas for compounds 3 and 7 there was only a small change in the absorption maxima, although there were significantly larger oscillator strengths for the longer wavelength absorptions. The increase in intensity of the long wavelength absorption tail in the solid state could be due to aggregation and/or scattering affects caused by the microcrystalline structure of the films in the case of 2 and 3.

We next studied the photoluminescence properties of the materials. The solution PL spectra were all broad and featureless and there was a red shift in the peak of the PL emission in moving from 2 to 3, which is consistent with the difference observed in the absorption spectra. Interestingly, in spite of 3 and 7 having similar absorption spectra the peak of the PL of



Fig. 9 Normalised absorbance and photoluminescence spectra of compounds 2, 3 and 7 in dichloromethane (solid lines) and thin films (dashed lines).

the latter is also further red shifted. In moving to the solid state there is a slight narrowing of the PL spectra, which can be ascribed to a decrease in conformational freedom and in the case of 2 and 3 there is a small red shift in the PL peak. The PL quantum yields (PLQY) in solution and the solid state showed that all three compounds were weakly emissive (see Table 3), which is consistent with  $S_1 \rightarrow S_0$  being a forbidden transition. The PL decays of compounds 2 and 3 in solution were near identical with lifetimes of approximately 1.6 ns (Fig. 10). In contrast, the decay of 7 was faster than the time resolution of our instrument. A similar compound to 7 has been previously reported to have a lifetime of 0.45 ns in 1,2-dichlorobenzene.19 From the values of the PLQY and excited state lifetimes the radiative and non-radiative decay rates were calculated with the results given in Table 3. These show that compounds 2 and 3 have radiative decay rates of order  $10^{-6}$  s<sup>-1</sup>, which is considerably slower than those reported for DPPs ( $\approx 10^{-8} \text{ s}^{-1}$ )<sup>21</sup> and consistent with the S1 transition having weak oscillator strength. The PLQY and lifetime measurements were repeated with degassed dichloromethane but there were no significant differences observed.

Measurements of the solid state PLQY show that both 2 and 3 were about as luminescent as they were in solution, with 7



10<sup>0</sup>

10

 $10^{-2}$ 

10

10

PL Intensity (norm.)



Fig. 10 Time-resolved photoluminescence decays of compounds 2, 3 and 7 in solution (empty circles) and the solid-state (filled circles). The PL decay of 2 was measured with excitation at 372 nm, and 3 and 7 at 441 nm.

being about an order of magnitude larger. The PL decay of compound 2 showed a short-lived component with the same decay lifetime as the emission in solution but also featured a long-lived component. The long-lived component, which was also measured at longer timescales, could be described in terms of two decay components of 115 ns and 770 ns with equal weighting. Long-lived decay components can arise from aggregate and/or excimer emission, or indeed phosphorescence. From the crystal structure and GIWAX measurements of 2 we can see that the closest  $\pi$ - $\pi$  interactions occur between the

Table 3     The optical properties of compounds 2, 3, and 7									
Compound	Solution				Film				
	PLQY	$\tau$ (ns)	$k_{ m R} \left( { m s}^{-1}  ight)$	$k_{ m NR} \left( { m s}^{-1}  ight)$	PLQY	$\tau$ (ns)	$k_{ m R} \left( { m s}^{-1}  ight)$	$k_{ m NR} \left( { m s}^{-1}  ight)$	
2	0.0045(5)	1.54	$2.9 imes 10^6$	$6.4 imes10^8$	0.006(1)	_	_	_	
3	0.011(1)	1.66	$6.6\times10^{6}$	$6.0 imes10^8$	0.009(1)	1.62	$5.6\times10^{6}$	$6.1 imes10^8$	
7	0.00035(5)	_	_	_	0.003(1)	0.97	$3.1 imes10^6$	$1.0 imes10^9$	

phenyl side groups, which from our calculations have orbital density, and hence is consistent with intermolecular chromophore-chromophore interactions (aggregate and/or excimer emission) from the microcrystalline film of 2. Furthermore, the GIWAX measurement indicates that there are two crystal forms, which is could give rise to the two distinct lifetimes. The PL decay of 3 was found to be near identical to that measured in solution with a lifetime of about 1.6 ns, which suggests that intermolecular interactions in the solid state are weaker. This is not entirely consistent with the X-ray data but may arise from the greater orientational disorder that is observed in the GIWAXS. The excited state lifetime of 7 in the solid state follows a monoexponential decay with a lifetime of about 1 ns (Fig. 10), which is longer than the decay in solution. The GIWAX measurements on films of 7 show that there is some short range ordering suggesting that the increase in lifetime is at least in part due to interchromophore interactions leading to aggregate or excimer emission.

To better understand the radiative and non-radiative processes we carried out photoinduced absorption (PIA) spectroscopy on thin films with the spectrum plotted in Fig. 11 for 2. In Fig. 11 it can be seen that there is a broad photoinduced absorption signal with a peak around 2.1 eV, which could be caused by triplet exciton or polaron absorption. A similar feature for 3 and 7 could be partially observed – the signal occurred at similar energies to the PL and so could not be fully resolved. The lifetime of the excited state was determined by



Fig. 11 (a) Photo-induced absorption spectrum of compound 2 in the solid state at room temperature. (b) Pump modulation dependence of the PIA signal at 2.1 eV (circles) with a fit to the data with eqn (1) (solid line).

measuring the change in the PIA signal with modulation of the pump frequency. The observed decrease in PIA signal  $(\Delta T/T)$  with increasing frequency was fitted with

$$-\frac{\Delta T}{T} = \frac{\left(-\frac{\Delta T}{T}\right)_{\omega=0}}{1+\omega\tau} \tag{1}$$

where  $\omega$  is the modulation frequency and  $\tau$  is the lifetime of the excited state. Fits to the data gave a lifetime of the excited state absorption of 0.4 ms, which is much longer than the lifetime of the photoluminescence signal and consistent with a triplet state.

Drawing all the measurements together gives a clear picture of the basic photophysics of the isoDPP compounds. In the solution and solid state excitation is primarily to  $S_2$  in 2 and 3 and  $S_5$  in 7 as these states have the highest oscillator strengths. In solution there is rapid relaxation *via* phonon coupling to  $S_1$ , which cannot relax rapidly to the ground state due to the transition being dipole forbidden. As a consequence the radiative rate is two orders of magnitude less than the non-radiative rate. In the solid state a similar process occurs although aggregation opens up new channels for relaxation of the excited state. Furthermore, we have observed intersystem crossing to the triplet state occurs in the films, and it would be reasonable to expect that this also contributes to the non-radiative rate in solution.

## Conclusion

In summary, we have studied a new class of pyrrolo[3,2-b]pyrrole-1,4-dione (isoDPP) compounds. We have investigated the effect of changing the aromatic ring (thiophene for phenyl) as well as the addition of alkoxy chains, on the molecular packing and on the optical/photophysical properties. We found that changing to a thiophene ring had a crucial effect on the molecular packing by reducing the  $\varphi$ C twisting angle and thus slightly planarizing the overall structure. The compounds without an alkyl chain (compounds 2 and 3) possessed poor solubility in common organic solvents but have good thermal stability. Finally, all the compounds are weakly fluorescent in both solution and solid state with PLQYs <1%. This present study provides essential information about this new class of material (isoDPP) that can be applied to the design of new polymeric materials for applications in devices such as organic photovoltaic cells.

## Experimental

### General

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a 400 or 500 MHz Bruker spectrometer in appropriate deuterated solvents at 298 K. Chemical shifts were reported as  $\delta$  values (ppm) relative to the residual solvent signals [(CDCl<sub>3</sub>) 7.26 ppm; (DMF- $d_7$ ) 8.02 ppm] and coupling constants are given to the nearest 0.5 Hz. Note: the lack of solubility of compounds 2 and 3 in CDCl<sub>3</sub> or DMF- $d_7$  precluded their <sup>13</sup>C NMR spectra being measured. UV-visible spectroscopy was performed on a Cary 5000 UV-Vis

spectrophotometer as either a thin film on quartz or as a solution in spectroscopic grade solvent (DCM = dichloromethane, ODCB = 1,2-dichlorobenzene). For compounds 2 and 3, the solvent was heated to boiling point, cooled and the absorption spectrum was measured. FT-IR spectroscopy was performed on solid samples using a Perkin-Elmer Spectrum 100 FT-IR Spectrometer with an ATR attachment. Melting points (mp) were measured in a glass capillary on a Buchi B-545 melting point apparatus and are uncorrected. Microanalyses were carried out on a Carlo Erba NA 1500 Elemental Analyser. Electrospray ionisation (ESI) and electron ionization (EI) mass spectrometry was carried out on a BRUKER HCT 3D Ion Trap mass spectrometer. Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer STA 6000 Simultaneous Thermal Analyser apparatus at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. Thermal decomposition values were reported as the temperature corresponding to a 5% reduction in weight  $(T_d)$ . Differential scanning calorimetry (DSC) was carried out with a Perkin-Elmer Diamond Differential Scanning Calorimeter at a heating/ cooling rate of 50 °C min<sup>-1</sup>. X-ray crystallography (XRD) was carried out on single crystals of compounds 2, 3 and 7 by Professor Paul Bernhardt using an Oxford Diffraction Gemini Ultra dual source (Mo and Cu) CCD Diffractometer. Transmission optical microscopy was carried out with an Olympus BX61 polarizing microscope. Column chromatography was performed with Kieselgel 60 230-400 mesh silica purchased from Merck. Thin layer chromatography (TLC) was performed on aluminum plates coated with silica gel 60 F254. Photoelectron Spectroscopy in Air (PESA) measurements were performed using a Riken Kekei AC-2 spectrometer. For all samples a power intensity of 5 nW was used. The spectral data for compound 2 and 3 was collected from the same batch of crystals as used for the crystal structure determination. Prior to NMR analysis 2 and 3 in DMF- $d_7$  were heated at reflux and then allowed to cool. On cooling a proportion of the material precipitated and the spectrum was collected on the soluble fraction. As a consequence some small baseline peaks were observed in the NMR and the peaks quoted are for the compounds themselves.

#### Materials

All commercial reagents were purchased from Aldrich, Alfa Aesar, Scharlau or Ajax Finechem and used as received unless otherwise noted. Molecular sieves (4 Å and 3 Å) were activated for use by heating at 200 °C under vacuum ( $10^{-1}$  to  $10^{-2}$  mbar) for 24 h. All solvents were distilled prior to use. Tetrahydrofuran was distilled from sodium and benzophenone under a nitrogen atmosphere before use. (1Z,2Z)-N',N''-Diphenyloxalimidoyl dichloride 1,<sup>22</sup> and 4-(n-hexyloxy)aniline 4,<sup>23</sup> were synthesized as described in the literature.

### Density functional calculations

Density functional calculations were performed using the measured crystal structures of compounds 2, 3, and 7 with proton positions determined by a geometry optimization performed using GAMESS<sup>24</sup> using the B3LYP hybrid functional<sup>25</sup> and the Pople 6-31G basis set. The *n*-hexyloxy chains have been

approximated by a methoxy to reduce the computational time. For comparison we also repeated the calculations with full relaxed geometries and only small changes were found.

Time dependent DFT (TDDFT) calculations were carried out with the Amsterdam Density Functional (ADF) 2013.01 program<sup>26</sup> in a triple zeta plus polarization (TZP) basis of Slater orbitals, using a 'small' core and the B3LYP functional. For internal consistency we used the DFT results obtained in the initial stages of this calculation to report the molecular orbital energies and wavefunctions throughout this manuscript.

#### Steady-state spectroscopy

The photoluminescence spectra of the compounds in dichloromethane were measured with a Fluoromax 4 by exciting the compounds at the peak absorbance. The solution PLQY measurements were performed using the relative method with quinine sulphate in 0.5 M  $H_2SO_4$  as the standard (PLQY = 54.6%).27 The materials were excited at 360 nm. In the case of compound 7 the PLQY was estimated relative to compound 3 as the emission was significantly lower in intensity than that of quinine sulphate. Films were prepared by evaporation onto fused silica substrates. Films with thicknesses of 85-120 nm were used for the absorbance measurements, PL spectra and PL lifetime, and films of 150-160 nm were used for measuring the PLQY and PIA. The PL spectra were measured with the films under vacuum and excited with the 442 nm output from a HeCd laser. The emission was directed into an Acton SpectraPro 2300i monochromator with a silicon photodiode used to measure the PL spectrum, which was corrected for the wavelength response of the system. The PLQY were measured using the method described by Greenham et al.28 The films were placed inside an integrating sphere, the interior of which was flushed with nitrogen, and excited with either the 325 nm (compound 2) or 442 nm (compounds 3 and 7) output of a HeCd laser with a power of  $\approx 0.2$  mW incident on the film.

#### Time-resolved photoluminescence spectroscopy

The PL decays were measured with a Fluorolog 4 with TCSPC capability. Pulsed LEDs emitting at 372 nm (compound 2) or 441 nm (compounds 3 and 7) were used to photoexcite the solutions and films. Films were stored in a sealed optical chamber in a nitrogen atmosphere for the measurements. Fits to the data were performed following convolution with the instrument response function (IRF), which was measured separately with a Ludox solution.

#### Photoinduced absorption spectroscopy

The 325 nm output of the HeCd laser was used as the pump with the output from a halogen lamp *via* a monochromator as the probe. A mechanical chopper was used to modulate the pump at  $\approx$  180 Hz with the photoluminescence and photoinduced absorption signals detected with a silicon photodiode coupled to a second monochromator with a phase-matched lock-in amplifier. The films were stored in an inert atmosphere for the duration of the measurement. The diameter of the

pump beam at the sample was approximately 1 mm with a power of  $\approx 10$  mW.

#### Grazing-incidence wide-angle X-ray scattering (GIWAXS)

Measurements were performed at the SAXS/WAXS beamline at the Australian Synchrotron. 11 keV Photons were used with 2D scattering patterns recorded on a Pilatus 1M detector. The sample-to-detector distance was calibrated using a silver behenate standard. Scattering patterns were recorded as a function of X-ray angle of incidence, with the angle of incidence varied from 0.05 degrees below the critical angle of the organic film to 0.2 degrees above the critical angle. The images reported were taken at an angle of 0.01 degrees above the critical angle. Data acquisition times of 3 s were used, with three 1 s exposures taken with offset detector positions to cover gaps in the Pilatus detector. X-ray diffraction data are expressed as function of the scattering vector, *q*, that has a magnitude of  $(4\pi/\lambda)\sin(\theta)$ , where  $\theta$  is half the scattering angle and  $\lambda$  is the wavelength of the incident radiation.

### Synthesis of 1,3,4,6-tetraphenylpyrrolo[3,2-*b*]pyrrole-2,5(1*H*,4*H*)-dione (2)

Oxalyl chloride (1.9 cm<sup>3</sup>, 22 mmol) was added to a solution of aniline (4.0 g, 21 mmol) in dry toluene (32 cm<sup>3</sup>) over 10 min. A slurry formed and the mixture was stirred for 20 min at room temperature. Then phosphorus pentachloride (9.4 g, 45 mmol) was added at room temperature. The mixture was carefully heated to reflux and kept at reflux until no more gas was generated. The orange mixture was then cooled down to room temperature and the solvent evaporated under reduced pressure. Petroleum ether (400 cm<sup>3</sup>) was added and the precipitate filtered and discarded. The petroleum filtrate was collected and the solvent removed. The resulting solid 1 (1.50 g) was used directly (within a 3 h period) without any further purification. n-Butyllithium (1.55 M, 9.2 cm<sup>3</sup>, 14 mmol) was added to a tetrahydrofuran (10 cm<sup>3</sup>) solution of di-*iso*-propylamine (2.2 cm<sup>3</sup>, 16 mmol) cooled in an acetone/dry ice bath. After stirring for 30 minutes, a tetrahydrofuran (50 cm<sup>3</sup>) solution of ethyl-2-phenylacetate (2.05 g, 12 mmol) was added slowly. The reaction mixture was then stirred for 1 h. 1 (1.5 g, 5.4 mmol) in tetrahydrofuran (30 cm<sup>3</sup>) was then added dropwise to the stirred reaction mixture, which was cooled in a acetone/dry ice bath. The solution was allowed to warm to room temperature and then stirred for 14 h. The mixture was poured into aqueous ammonium chloride (5 M, 300 cm<sup>3</sup>). The addition of ether (300 cm<sup>3</sup>) resulted in the formation of a precipitate, which was collected at the filter. The precipitate was washed with water (300 cm<sup>3</sup>) and ether (300 cm<sup>3</sup>). The solid was then dried under high vacuum. The product was recrystallised three times from N,N-dimethylformamide to afford yellow-orange needles of 2 (1.25 g, 54% over two steps); mp 348 °C; found: C, 81.7%, H, 4.6%, N, 6.3%; C<sub>30</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> requires C, 81.8%, H, 4.6%, N, 6.4%; IR  $\nu_{\text{max}}$  (solid)/cm<sup>-1</sup> 1722 (CO);  $\lambda_{\text{max}}$  (ODCB)/nm 353 [log( $\varepsilon$ /dm<sup>3</sup>  $mol^{-1} cm^{-1}$ ) (4.07)] 429sh (2.23);  $\delta_{\rm H}$  (500 MHz; DMF- $d_7$ ) 7.14– 7.19 (8H, m, Ph-H), 7.23-7.27 (2H, m, Ph-H), 7.28-7.32 (4H, m, Ph-H), 7.33–7.36 (6H, m, Ph-H); m/z (EI) found 440.2 (100%),

441.2 (35%), 442.2 (6%) [M<sup>+</sup>];  $C_{30}H_{20}N_2O_2$  requires 440.15 (100%), 441.16 (33%), 442.16 (6%).

### Synthesis of 1,4-diphenyl-3,6-di(thiophen-2-yl)pyrrolo[3,2-*b*]pyrrole-2,5(1*H*,4*H*)-dione (3)

n-Butyllithium (1.55 M, 1.84 cm<sup>3</sup>, 2.85 mmol) was added to a tetrahydrofuran (2 cm<sup>3</sup>) solution of di-iso-propylamine (0.44 cm<sup>3</sup>, 3.18 mmol) cooled in an acetone/dry ice bath. After stirring for 30 min, a tetrahydrofuran (10 cm<sup>3</sup>) solution of ethyl-2-(thiophen-2-yl)acetate (0.40 g, 2.37 mmol) was added slowly. The reaction mixture was then stirred for 1 h with acetone/dry ice bath cooling. 1 (0.30 g, 1.08 mmol) in tetrahydrofuran (6 cm<sup>3</sup>) was added dropwise to the stirred reaction mixture, which was cooled in an acetone/dry ice bath. The solution was allowed to warm to room temperature, and stirred for 14 h. The mixture was poured into aqueous ammonium chloride (5 M, 100 cm<sup>3</sup>). The addition of ether (300 cm<sup>3</sup>) resulted in the formation of a precipitate, which was collected at the filter. The precipitate was washed with water  $(200 \text{ cm}^3)$  and ether (200 cm<sup>3</sup>). The solid was then dried under high vacuum. The product was recrystallised twice from N,N-dimethylformamide to afford red needles of 3 (190 mg, 39% over two steps): mp > 350 °C; found C, 68.6%, H, 3.6%, N, 6.4%, S, 14.0%; C<sub>26</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> requires C, 69.0%, H, 3.6%, N, 6.2%, S: 14.1%; IR  $\nu_{max}$  (neat)/cm<sup>-1</sup> 1717 (CO);  $\lambda_{max}$  (ODCB)/nm 415 [log( $\epsilon$ /dm<sup>3</sup>  ${
m mol}^{-1}~{
m cm}^{-1}$ ) (3.65)];  $\delta_{
m H}$  (500 MHz; DMF- $d_7$ ) 6.44 (2H, dd, J=3.5 Hz, I = 1.0 Hz, Th-H, 6.88 (2H, dd, I = 5.0 Hz, I = 3.5 Hz, Th-H), 7.50–7.55 (10H, m, Ph-H), 7.62 (2H, dd, J = 5.0 Hz, J = 1.0 Hz, Th-H); m/z (HR-ESI) found 453.0726 (100%) 454.0783 (33%), 455.0704 (13%), 456.0690 (3%) [M + H]; C<sub>26</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> requires 453.0726 (100%), 453.0759 (28%), 455.0687 (9%), 456.0718 (4%).

#### Synthesis of N', N''-bis(4-(hexyloxy)phenyl)oxalamide (5)

Oxalyl chloride (2.15 g, 16.9 mmol) was added dropwise to a stirred solution of 4 (6.87 g, 35.5 mmol) and triethylamine (4.28 g, 42.3 mmol) in tetrahydrofuran (120 cm<sup>3</sup>) cooled with an ice bath. The reaction was then allowed to warm to room temperature with stirring over 2 h. Water (120 cm<sup>3</sup>) was added to the reaction mixture and the white precipitate was collected at the filter, washed with aqueous hydrochloric acid (1 M, 100 cm<sup>3</sup>) and then water (200 cm<sup>3</sup>). The product was then dried in a drying pistol at 50 °C under high vacuum to afford a white powder of 5 (4.87 g, 65%): mp 218 °C; found C, 71.1%, H, 6.0%, N, 8.2%; C<sub>26</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub> requires C, 70.9%, H, 6.3%, N, 8.2%; IR  $\nu_{\rm max}$  (solid)/cm<sup>-1</sup> 3298 (NH), 1650 (CO);  $\lambda_{\rm max}$  (DCM)/nm 295  $[\log(\epsilon/dm^3 mol^{-1} cm^{-1})$  (4.29)] 299sh (4.28), 318sh (4.17);  $\delta_{\rm H}$ (400 MHz; CDCl<sub>3</sub>) 0.90-0.95 (6H, m, -CH<sub>3</sub>), 1.32-1.40 (8H, m, -CH<sub>2</sub>-), 1.41-1.51 (4H, m, -CH<sub>2</sub>-), 1.77-1.83 (4H, m, -CH<sub>2</sub>-), 3.96 (4H, t, J = 6.5 Hz, -OCH<sub>2</sub>-), 6.91 and 7.57 (8H, AA'BB', Ph-H), 9.25 (2H, brs, N–H);  $\delta_{\rm C}$  (100 MHz; CDCl<sub>3</sub>) 14.0, 22.6, 25.7, 29.2, 31.6, 68.3, 115.0, 121.3, 129.3, 156.8, 157.3; m/z (ESI) found 463.2567 (100%), 464.2603 (29%), 465.2680 (5%), [M + Na]; C<sub>26</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>Na requires 463.2573 (100%), 464.2606 (28%), 465.2640 (4%).

### Synthesis of 1,4-bis(4-(hexyloxy)phenyl)-3,6-di(thiophen-2-yl)pyrrolo[3,2-*b*]pyrrole-2,5(1*H*,4*H*)-dione (7)

Phosphorus pentachloride (0.90 g, 4.29 mmol) was added to a solution of N', N''-bis(4-(hexyloxy)phenyl)oxalamide 5 (0.90 g, 2.04 mmol) in anhydrous toluene (15 cm<sup>3</sup>) stirred at room temperature under an argon atmosphere. The mixture was carefully heated to reflux and kept at reflux until no more gas was generated. The orange mixture was then allowed to cool to room temperature and the solvent removed under reduced pressure. Petroleum ether (200 cm<sup>3</sup>) was added and the precipitate was removed by filtration and discarded. The filtrate was collected and the solvent removed. The resulting solid of 6  $(\approx 1.80 \text{ g})$  was used directly (within a 3 h period) without further purification. n-Butyllithium (1.55 M, 6.94 mL, 10.8 mmol) was added to a tetrahydrofuran solution (10 cm<sup>3</sup>) of di-iso-propylamine (1.20 g, 11.8 mmol) cooled in an acetone/dry ice bath. After stirring for 30 min, a tetrahydrofuran (40 cm<sup>3</sup>) solution of ethyl-2-(thiophen-2-yl)acetate (1.54 g, 8.98 mmol) was added slowly with the reaction mixture being cooled in an acetone/dry ice bath. (1Z,2Z)-N',N''-Bis[4-(*n*-hexyloxy)phenyl]oxalimidoyl dichloride 6 (1.80 g, 4.08 mmol) in tetrahydrofuran (16 cm<sup>3</sup>) was then added dropwise to the stirred reaction mixture before it was allowed to slowly warm to room temperature. The reaction was stirred for a further 16 h before being poured into aqueous ammonium chloride (5 M, 300 cm<sup>3</sup>). Diethyl ether (300 cm<sup>3</sup>) was added to the mixture resulting in the formation of a precipitate. The precipitate was collected at the filter, and then washed with water (200 cm<sup>3</sup>) followed by diethyl ether (150 cm<sup>3</sup>). The solid was then dried in an oven at 80 °C for 2 h. The orange solid was then purified by column chromatography over silica using dichloromethane : hexane mixture (1:1) as the eluent to give an orange solid of 7 (1.05 g, 36% over two steps): mp 249 °C; found C, 69.6%, H, 6.1%, N, 4.3%, S, 9.7%; C<sub>38</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> requires C, 69.9%, H, 6.2%, N, 4.3%, S: 9.8%; IR  $\nu_{\rm max}$  (solid)/ cm<sup>-1</sup> 1724 (CO);  $\lambda_{max}$  (ODCB)/nm 415  $[log(\epsilon/dm^3 mol^{-1} cm^{-1})]$ (4.39)];  $\delta_{\rm H}$  (400 MHz; CDCl<sub>3</sub>) 0.90–0.97 (6H, m, -CH<sub>3</sub>), 1.33–1.42 (8H, m, -CH<sub>2</sub>-), 1.44-1.54 (4H, m, -CH<sub>2</sub>-), 1.77-1.87 (4H, m, -CH<sub>2</sub>-), 3.99 (4H, t, J = 6.6 Hz, -OCH<sub>2</sub>-), 6.57 (2H, dd, J = 4.0 Hz, J = 1.0 Hz, Th-H), 6.80 (2H, dd, J = 5.0 Hz, J = 4.0 Hz, Th-H), 6.92 and 7.22 (8H, AA'BB', Ph-H), 7.27 (2H, dd, J = 5.0 Hz, J = 1.0 Hz, Th-H);  $\delta_{\rm C}$  (100 MHz; CDCl<sub>3</sub>) 14.0, 22.6, 25.7, 29.1, 31.6, 68.4, 100.4, 114.8, 126.3, 126.6, 128.2, 128.5, 129.5, 129.7, 142.5, 159.0, 170.6; m/z (ESI) found 652.2 (100%), 653.2 (54%), 654.1 (26%), 655.2 (9%) [M]; C<sub>38</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> requires 652.2 (100%), 653.2 (42%), 654.3 (10%), 654.2 (9%).

# Acknowledgements

P.L.B. is supported by a University of Queensland Vice Chancellor's Senior Research Fellowship. B.J.P. is supported by an Australian Research Council Future Fellowship (FT130100161). We acknowledge support from The University of Queensland (Strategic Initiative – Centre for Organic Photonics & Electronics). This Program has been supported in part by the Australian Government through the Australian Renewable Energy Agency (ARENA). Responsibility for the views, information or advice expressed herein is not accepted by the Australian Government. P.E.S. is supported by an Australian Research Council Discovery Early Career Researcher Award (DE120101721). F.M. acknowledges The University of Queensland for UQ Centennial and UQ International Scholarships. C.R.M. acknowledges support from the Australian Research Council (FT100100275, DP130102616). This research was undertaken in part on the SAXS/WAXS beamline at the Australian Synchrotron, Victoria, Australia.

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