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Full Paper

# Effect of Extended Conjugation on the Optoelectronic Properties of Benzo[1,2-*d*:4,5-*d*']bisoxazole Polymers

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Four copolymers comprising benzo[1,2-d:4,5-d']bisoxazole (BBO) and benzo[1,2-b:4,5-b']dithiophene (BDT) bearing phenylethynyl substituents on either the BBO, BDT moieties or both units were synthesised and the influence of twodimensional conjugation on their optoelectronic properties investigated. Extending conjugation along the BBO resulted in a 0.5 eV decrease in the LUMO level, whereas the HOMO level was raised by 0.2 eV. Extending conjugation across the BDT moiety in also resulted in a 0.5 eV decrease in the LUMO level, however, the effect was negligible on the HOMO level. Thus, cross-conjugation can be used to independently tune the LUMO level within these systems.

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### Introduction

In recent years there has been a large amount of research devoted to the development of organic semiconductors OSCs as replacements for conventional inorganic materials.<sup>[1]</sup> These materials have been applied in several areas such as field effect transistors,<sup>[2]</sup> organic light-emitting diodes,<sup>[3]</sup> and organic photovoltaic cells.<sup>[4]</sup> OSCs offer several advantages over inorganic semiconductors, including ease of preparation in solution,<sup>[5]</sup> which can reduce fabrication costs and facilitate tuning of the optoelectronic properties through chemical synthesis. Generally, the introduction of flexible side chains in the conjugated polymer backbone not only improves the solubility and film-forming characteristics, but also influences the nanoscale morphology, and the electronic, optical, and physical properties.<sup>[6]</sup> Varying the electron-donating or electronaccepting strength of the arenes along the polymer backbone can further modify the optical and electronic properties of these materials. Thus, in principle, OSCs featuring highest occupied molecular orbitals (HOMOs), lowest unoccupied molecular orbitals (LUMOs), and band gaps that are tailored to specific applications can be synthesised. Unfortunately, in practice, this is often difficult to accomplish because of the complex interplay between the structure of the material and its properties, resulting from the extensive delocalisation of electrons within the OSCs. Therefore, synthetic strategies that facilitate the independent tuning of the HOMO and LUMO levels are highly sought after.

To this effect, 2-dimensional cross-shaped 'cruciform' molecules that feature two conjugation axes are particularly promising. These compounds have spatially segregated frontier molecular orbitals (FMOs) that facilitate the individual modification of either the LUMO or the HOMO by changing the substituents and their location on the central molecule.<sup>[7]</sup> Although there have been many reports on the synthesis of cruciform small molecules,<sup>[7,8]</sup> reports on the effect of extended conjugation in polymeric systems are limited, whereby many of them are based on copolymers of benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) derivatives featuring extended conjugation.<sup>[9]</sup> BDT is an electron-rich molecule that has been widely investigated for the synthesis of conjugated polymers because it has a planar, conjugated structure that facilitates  $\pi$ – $\pi$  stacking and promotes charge carrier mobility.<sup>[10]</sup> As a result, power conversion efficiencies of polymer solar cells, involving BDT copolymers, have exceeded 9 %.<sup>[10c,11]</sup> By replacing the electron-rich alkoxy groups with thien-2-yl, aryl, alkynyl, and phenylethynyl groups on the 4- and 8-positions of the BDT moiety, the HOMO level can be lowered.

Similarly, benzo[1,2-*d*:4,5-*d*']bisoxazole BBOs are electron deficient moieties that have been incorporated in polymers with exceptional thermal and chemical stability,<sup>[12]</sup> efficient electron transport, and blue emission.<sup>[13]</sup> [<sup>14]</sup> Similarly to BDT, BBO can be substituted at the 4- and 8-positions with aryl, alkynyl, and phenylethynyl groups.<sup>[8a,15]</sup> It has been demonstrated that the HOMO and LUMO levels of BBO in small molecules could readily be tuned by substitution<sup>[7d,16]</sup> and that the resulting effect on the energy levels is dependent on the nature and location of the substituent.<sup>[8a]</sup> However, the effect of extended conjugation on the HOMO, LUMO, and the band gap of BBO-based polymers is yet to be explored. Herein, we synthesised four new polymers using a combination of one- and two-dimensional BDT and BBO monomers. The effect of the extended conjugation on the optoelectronic properties was evaluated using cyclic voltammetry, UV–Vis spectroscopy, and density functional theory (DFT).

### **Results and Discussion**

### Synthesis of BBO monomers

Previously, we reported the synthesis of 2,6-(dithien-2-yl) BBOs via the Lewis-acid catalysed condensation of diamino diols and aryl orthoesters.<sup>[17]</sup> A similar approach was herein used for the synthesis of the BBO monomer. Orthoester **1** (Scheme 1) was first synthesised from 2-bromo-3-(2-ethylhexyl)thiophene<sup>[18]</sup> in 54 % yield using the method first reported by Tschitschibabin.<sup>[17,19]</sup> This alkyl substituent was used to increase the solubility of the BBO monomers and facilitate bromination at the 5-position. Furthermore, location of the alkyl chain at the 3-position instead of the 4-position on thiophene is expected to decrease steric interactions between the monomer units in the polymer and steric hindrance during polymerisation. The reaction between **1** and 2,5-diamino-1,4-hydroquinone bishydrochloride (DAHQ)<sup>[20]</sup> afforded BBO **2** in 55 % yield (Scheme 2). This yield was lower than our previous reports using similar compounds, and was likely because of



Scheme 1. Synthesis of substituted orthoester 1.

steric hindrance exerted by the 2-ethylhexyl chain adjacent the trimethoxymethyl moiety. BBO **2** was then easily brominated in 69 % yield to give one-dimensional BBO monomer **3**.

A similar approach was used to synthesise the two-dimensional BBO monomer and is outlined in Scheme 3. The condensation reaction between 1 and 3,6-diamino-2,5-dibromo-1,4-hydroquinone<sup>[21]</sup> (Br-DAHQ) afforded BBO 4 in 19% yield. The lower yield of the reaction compared with that of 2 is likely because of the reduced nucleophilicity of Br-DAHQ. The two-dimensional BBO intermediate 5 was obtained from the Sonogashira coupling between 4 and 3,5-di-(2-ethylhexyloxy)-1-ethynylbenzene 6 in 91% yield (Scheme 4). The alkyne was easily synthesised from 3,5-di-(2-ethylhexyloxy)benzalde-hyde<sup>[22]</sup> via the Corey–Fuchs reaction. This alkyne was used



Scheme 4. Synthesis of substituted alkyne 6.



Scheme 2. Synthesis of linear BBO 3.



Scheme 3. Synthesis of two-dimensional BBO monomer 7.

because it enabled the introduction of long-branched alkyl chains for solubility purposes, whereas the *meta*-substitution pattern prevented electron-donation from the oxygen atoms to the BBO. Because electrophilic brominating reagents could not be used on BBO **5**, a double lithium–hydrogen exchange, using *n*-butyl lithium and N,N-N',N'-tetramethylethylenediamine (TMEDA) was performed, and quenching the resulting anion with carbon tetrabromide produced the target two-dimensional BBO monomer **7** in 62 % yield.

### Synthesis of BDT Monomers

The synthesis of both the one-dimensional and two-dimensional BDT monomers is shown in Scheme 5. The one-dimensional intermediate **8** was synthesised from benzo[1,2-*b*:4,5-*b'*] dithiophene-4,8-dione<sup>[23]</sup> according to the reported procedure.<sup>[24]</sup> The two-dimensional BDT system was prepared by nucleophilic addition of lithiated **6** (via *n*-butyl lithium) to benzo [1,2-*b*:4,5-*b'*]dithiophene-4,8-dione. This intermediate was aromatised in situ to afford **9** in 49 % yield. Optimal results were obtained using a slight excess amount of the alkyne. Subsequent

stannylation of **8** and **9** afforded monomers **10** and **11** in yields of 66 % and 86 %, respectively. The identity of all the compounds was confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and high-resolution mass spectroscopy.

### Synthesis of Copolymers

The copolymers were synthesised using a Stille cross-coupling catalysed by Pd(PPh<sub>3</sub>)<sub>4</sub> in a solution of toluene and DMF as shown in Scheme 6. The isolated polymers **P1–P4** were obtained in 43 %–80 % yield and the structures are shown in Fig. 1. The polymers were characterised by gel permeation chromatography (GPC), UV–Vis spectroscopy, and cyclic voltametry. <sup>1</sup>H NMR spectra of the four polymers were consistent with the proposed structures. The molecular weights of **P1–P4** determined by GPC are shown in Table 1. The polymers showed good solubility in chlorinated solvents and toluene, and had moderate-to-high molecular weights that vary significantly. **P2** displayed the highest number average molecular weight ( $M_n$ ) i.e. 39000 Da and **P1** featured the lowest  $M_n$  i.e. 7000 Da. The low molecular weight of **P1** was due to the reduced number of



Scheme 5. Synthesis of BDT donors.



Scheme 6. Synthesis of polymers P1-P4.



Fig. 1. Structures of polymers P1-P4.



	$M_{\rm n}^{\rm A}$ [kDa]	PDI <sup>B</sup>	$DP_n^C$	$T_{\rm d}^{\rm D}  [^{\circ}{\rm C}]$
P1	7.02	1.17	7	359
P2	39.8	2.31	23	372
P3	28.9	1.44	20	412
P4	19.2	1.55	9	402

 $^{A}M_{n}$ : number average molecular weight.

<sup>B</sup>PDI:  $M_{\rm w}/M_{\rm n}$  where  $M_{\rm w}$  is the molecular weight.

<sup>c</sup>DP<sub>n</sub>: Degree of polymerisation based on  $M_n$ .

 $^{\rm D}T_{\rm d}$ : Temperature at which a 5 wt-% loss was observed, as determined by TGA in air.

side chains and prominent rigid rod-like structure when compared with those of the remaining polymers, allowing for increased  $\pi-\pi$  stacking. In the case of **P4**, the large size of the two-dimensional monomers likely contributed to its reduced  $M_n$ . The general increase in  $M_n$  for the cross-conjugated polymers **P2–P4** was likely because of the increased steric bulk of the phenylacetylene side chains and increased side-chain density that disrupted  $\pi-\pi$  stacking.

The thermal properties of the polymers were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Based on the DSC analysis, none of the polymers displayed transitions below 300°C (Fig. S29), indicating the amorphous nature of the polymers. The polymers all showed excellent thermal stability: a 5 wt-% mass loss was observed at varying temperatures between 359°C (P1) and 412°C (P3) as determined by TGA in air (Fig. S30).

### Spectroscopic and Electronic Characterisation

The normalised absorption spectra of P1-P4 both as dilute CHCl<sub>3</sub> solutions and thin films are shown in Figs 2 and 3, respectively, and the optical data are summarised in Table 2. In comparison with the solution-based spectrum, the thin film-based spectrum of the unsubstituted polymer, P1, exhibits a



Fig. 2. Solution UV–Vis spectra of P1–P4 in chloroform.



Fig. 3. Thin film UV–Vis spectra of P1–P4.

slight broadening of the absorption band and a slight red shift in the absorption maximum. In contrast, the substituted polymers **P2**, **P3**, and **P4** displayed similar solution- and film-based spectra, indicating that  $\pi$ -stacking in the polymers in the solid state is not efficient, likely because of the bulky side chains. In both solution and film forms, all four polymers exhibit a single absorption band, with two peaks corresponding to the  $\pi$ - $\pi$ \* transition. However, all spectra lack the presence of the lowenergy band characteristic of intramolecular charge transfer

Table 2. Optical properties of BBO polymers

	$\lambda_{max}^{ m soln}$ [nm]	$\lambda_{max}^{\mathrm{film}}$ [nm]	$E_{\rm g}^{\rm opt} \left[ {\rm eV} \right]^{\rm A}$
P1	489, 525	493, 531	2.3
P2	504, 543	506, 539	2.2
P3	500, 538	506, 545	2.2
P4	492, 525	504, 542	2.2

<sup>A</sup>Calculated from the intersection between the thin film-based absorption and emission spectra (Fig. S25).

 Table 3. Experimental and theoretical comparison between the electronic properties of BBO polymers

	HOMO <sup>A</sup> [eV]		LUMO <sup>B</sup> [eV]		$E_{\rm g}^{\rm C}$ [eV]	
Polymer	Experiment	Theory	Experiment	Theory	Experiment	Theory
P1	-5.6	-4.98	-2.8	-2.68	2.8/2.3	1.94
P2	-5.4	-4.74	-3.2	-2.58	2.2/2.2	1.86
P3	-5.6	-4.86	-3.3	-2.63	2.3/2.2	1.88
P4	-5.6	-4.83	-3.3	-2.55	2.3/2.2	1.93

<sup>A</sup>Calculated from the oxidation onset using  $-(4.8 + E_{OX}^{onset})$ .

<sup>B</sup>Calculated from the reduction onset using  $-(4.8 + E_{red}^{onset})$ .

<sup>C</sup>The data are displayed as  $E_g^{EC}/E_g^{opt}$  where  $E_g^{EC}LUMO - HOMO$  and  $E_g^{opt}$  was calculated from the intersection between the thin film-based absorption and emission spectra.

(ICT) between the electron-donating and electron-accepting units within the polymer backbone.  $^{\left[25\right]}$ 

The electrochemical properties of the polymers were investigated using cyclic voltammetry and the profiles are shown in Fig. S23 (Supplementary Material). All four polymers exhibited measurable and reproducible oxidation and reduction processes. The HOMO and LUMO levels were estimated from the onset of the oxidation and reduction processes, respectively, using the absolute energy level of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as 4.8 eV under vacuum; the results are summarised in Table 3.<sup>[26]</sup> The unsubstituted polymer P1 has a HOMO level of -5.6 eVand a LUMO level of -2.8 eV, resulting in an electrochemical band gap of 2.8 eV. Extension of conjugation across the BBO moiety affords P2 with a slightly raised HOMO level at -5.4 eV, a lower LUMO level of -3.2 eV, and a narrower band gap of 2.2 eV. Likewise, extension of conjugation across the BDT moiety affords P3 with an unchanged HOMO level of -5.6 eV, a lower LUMO level of -3.3 eV, and an optical band gap of 2.3 eV. Interestingly, P4 that has extended conjugation across both the BBO and BDT moieties features the same HOMO and LUMO levels as those present in P3.

To further elucidate the influence of extended conjugation on the optical and electronic properties of these polymers, groundstate geometry optimisations (Fig. 4) were performed by DFT, employing a B3 LYP<sup>[27]</sup> functional, a 6-31G\* basis, and the Gaussian 09 software package.<sup>[28]</sup> Frontier molecular orbital (FMO) diagrams and electrostatic potential maps, as shown in Fig. 5, were generated from the DFT data. In addition, a timedependent DFT routine with the aforementioned functional and basis set was used to generate the excited states and the results are summarised in Table 3. According to DFT, the band gaps of polymers P1–P4 increased in the order of P2 < P3 < P4 < P1, although the difference between the values was only 0.08 eV. The calculated HOMO energy values of the polymers decreased in the order of P1 > P3 > P4 > P2; the difference between P3 and P4 was negligible. All of these observations agreed with the experimental data.



Fig. 4. Optimised geometries for model dimers of P1-P4.



Fig. 5. Electrostatic potential maps and FMO diagrams of P1-P4.

Copolymers that comprise alternating electron-donating and electron-accepting moieties have energy levels that are easily tuned by changing the strength of the donor and acceptor units. In these systems, the LUMO level is primarily related to the acceptor unit, whereas the HOMO level is largely determined by the donor unit.<sup>[29]</sup> Because the phenylethynyl BBO is a stronger acceptor than the unsubstituted BBO, extension of the conjugation with an electron-accepting phenylethynyl substituent across BBO is expected to lower the LUMO. Accordingly, P2 had a lower LUMO (by 0.5 eV) than P1 and P3, and it also had a slightly higher HOMO level (by 0.2 eV). This effect is likely a combination of the electron-accepting alkyne and the extended conjugation across BBO.<sup>[15]</sup> On the other hand, because phenylethynyl BDT is a weaker donor than unsubstituted BDT, extension of the conjugation along BDT is expected to lower the HOMO level. Hence, P3 is expected to have a lower HOMO level than P1 and P2, however, this was not observed. We believe that this is a result of twisting along the polymer backbone in P3, as demonstrated by the optimised geometry model dimers in this system. As seen in Fig. 4, the unsubstituted polymer **P1** is planar unlike the other polymers. Likewise, **P4** that has substituents on both BDT and BBO has the same HOMO, LUMO, and band gap values as those of P3 despite the presence of the second substituent. The optimised geometry for model dimers in this system also revealed significant twisting. Thus, the resulting energy levels are not merely a function of the increased electron density around the BBO and BDT moieties; steric effects also play a major role. The latter reduces the planarity of the system and decreases the delocalisation of electron density along the polymer backbone.

The FMO diagrams and electrostatic potential maps of all polymers indicate that the electron density is uniformly distributed along the polymer backbone. This further supports the experimental and theoretical findings that demonstrate that there is very little difference between the electronic properties of these polymers. Furthermore, the negligible difference between P3 and P4 can be attributed to the partial localisation of LUMO on the BDT moiety when compared with those of P1 and P2 that have complete delocalisation of the LUMO. These diagrams are consistent with the UV–Vis findings that show that

ICT is not occurring in these systems owing to the delocalisation of the FMOs.

### Conclusions

To experimentally and theoretically evaluate the use of crossconjugation for selectively modifying FMOs within conjugated polymers, three new two-dimensional polymers were synthesised and compared with the newly synthesised onedimensional polymer. The UV-Vis spectra of all polymers were similar, indicating that there were only minor differences between the optical properties of the polymers. Additionally, the comparable solution- and film-based spectra of P1-P4 indicated that there was little-to-no aggregation in the solid state, most likely because of steric effects introduced by the bulky side chains. However, the spectra of P1 indicated that ICT was not occurring within the polymer backbone, owing to the relative strength and weakness of the BDT donor and BBO acceptor, respectively. The extended conjugation of P2-P4 failed to increase ICT, as indicated by UV-Vis analysis and the lack of localisation of the electron density in the FMOs. The absence of donor-acceptor behaviour in the cross-conjugated polymers is partially a result of the steric twist along the polymer backbone, owing to the large side chains, along with the relative strength and weakness of the BDT donor and BBO acceptor, respectively. Nonetheless, the relatively constant HOMO level and modulation of the LUMO realised by structural modifications indicate that cross-conjugation is a promising approach for selectively tuning the LUMO level of OSCs. However, to further evaluate this approach, polymer design needs to be improved by using appropriate substituents to decrease steric interactions and realise stronger electron-rich monomers to promote ICT. Future work will focus on these alterations using experimental and theoretical methods.

#### **Experimental**

#### Characterisation

Nuclear magnetic resonance (NMR) experiments were carried out in CDCl<sub>3</sub> at 400 MHz (<sup>1</sup>H) or 100 MHz (<sup>13</sup>C) on a Varian MR-400. <sup>1</sup>H NMR spectra are internally referenced to the residually protonated solvent peak (7.26 ppm) and <sup>13</sup>C NMR spectra are referenced to the central carbon peak (77.16 ppm) of CDCl<sub>3</sub>. In all spectra, chemical shifts are given in  $\delta$  relative to tetramethylsilane. Coupling constants are reported in Hz. Highresolution mass spectra were recorded on a double-focusing magnetic sector mass spectrometer using electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI). Melting points were obtained on a melting point apparatus with a 260°C-upper limit and were uncorrected. Gel permeation chromatography (GPC) measurements were performed on a separation module equipped with three 5-µm I-gel columns connected in series (guard, high molecular weight, medium molecular weight, and low molecular weight) with a UV-Vis detector. Analyses were performed at 50°C using CHCl3 as the eluent at a flow rate of 1.0 mL min<sup>-1</sup> with calibration based on polystyrene standards. Electrochemistry was performed on a eDAQ e-Corder 410 using 0.01 M AgNO<sub>3</sub> in acetonitrile as the reference electrode, platinum wire as the counter electrode, and platinum button electrode as the working electrode at a scanning rate of  $50 \text{ mV s}^{-1}$ . All measurements were taken under argon atmosphere in deoxygenated acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte. The potentials measured versus Ag<sup>+</sup> were externally referenced to Fc/Fc<sup>+</sup> (-4.8 eV versus vacuum). Thermogravimetric analysis (TGA) measurements were performed over a temperature range of 25-800°C at a heating rate of 20°C min<sup>-1</sup> under ambient atmosphere. Differential scanning calorimetry (DSC) was performed using an initial scan at a heating rate of 10°C min<sup>-1</sup> followed by a second scan to evaluate transitions between 0 and 300°C under nitrogen. All sample films that were drop-cast from 1,2-dichlorobenzene solutions ( ${}^{o}DCB$ ,  $2 \text{ mg mL}^{-1}$ ) were annealed at 80°C under vacuum for 6 h before analysis. UV-Vis spectroscopy was performed on a Varian Cary Eclipse spectrometer on dilute chloroform solutions or thin films. Thin films were spin-coated from mixtures of chloroform and <sup>o</sup>DCB  $(5 \text{ mg mL}^{-1})$  onto  $25 \times 25 \times 1 \text{ mm}$  glass slides at 74 g on a Headway Research, Inc. PWM32 spin-coater and annealed at 80°C under vacuum for 6 h before analysis.

### Materials

Tetrabutylammonium hexafluorophospate was purchased from Oakwood Chemical and was recrystallised from methanol before use. All other chemicals were purchased from commercial sources and used without further purification. 2,5-Diamino-1,4-hydroquinone bishydrochloride (DAHQ),<sup>[20]</sup> 3,6-diamino-2,5-dibromo-1,4-hydroquinone (Br-DAHQ),<sup>[15]</sup> 2-bromo-3-(2-ethylhexyl)thiophene (7),<sup>[18]</sup> 3,5-bis(2-ethylhexyloxy)benz-aldehyde,<sup>[22]</sup> benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-dione,<sup>[23]</sup> and 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*: 4,5-*b*']dithiophene (8)<sup>[24]</sup> were synthesised according to literature procedures.

### General Synthetic Details

Unless otherwise noted, all reactions were carried out in ovendried glassware, under argon atmosphere, with stirring using standard Schlenk techniques. Column chromatography was carried out using silica gel  $(35-70 \,\mu\text{m})$  unless otherwise specified.

# *Synthesis* of 3-(2-ethylhexyl)-2-(triethoxymethyl) thiophene (1)

A dry two-neck flask equipped with an addition funnel and reflux condenser was filled with 1.22 g (50 mmol) magnesium

turnings and heated under vacuum at 90°C for 1 h. The flask was back-filled with argon and a few crystals of iodine were added and allowed to sublime for 20 min. The flask was cooled to room temperature and filled up with 35 mL dry diethyl ether (Et<sub>2</sub>O). Then, 4.6 mL (50 mmol) of 2-chloropropane in 10 mL dry Et<sub>2</sub>O was added dropwise using a funnel to maintain gentle reflux, and refluxed for an additional 1 h. A solution of 6.88 g (20.0 mmol) 2-bromo-3-(2-ethylhexyl)thiophene in 5 mL dry Et<sub>2</sub>O was added dropwise and the solution was refluxed for 24 h. The solution was cooled to room temperature prior to dropwise addition of 5.8 g (30 mmol) tetraethylorthocarbonate, and the reaction mixture was heated to reflux for 12 h. The reaction was then cooled to room temperature and poured in a cold saturated aqueous NH<sub>4</sub>Cl solution and the layers were separated. The aqueous layer was extracted with Et<sub>2</sub>O and the combined organic layers were washed with H2O and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was filtered and the solvent removed under vacuum. Low-boiling impurities were removed by Kugelrohr distillation to yield a yellow oil that was used without further purification (3.71 g, 54 %).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 7.17 (d, J 4, 1H), 6.89 (d, J4, 1H), 3.42 (q, J8, 6 H), 2.70 (dd, J4, 2H), 1.71 (m, J 8, 1H), 1.28–1.21 (comp, 8H), 1.21 (t, J 8, 9H), 0.87 (t, J 8, 6H). δ<sub>C</sub> (CDCl<sub>3</sub>) 140.5, 134.6, 129.4, 124.4, 113.5, 57.9, 39.5, 32.9, 32.7, 29.1, 26.0, 23.3, 15.0, 14.3, 11.0.

# 2,6-Bis(3-(2-ethylhexyl)thien-2-yl)benzo[1,2-d:4,5-d'] bisoxazole (**2**)

A dry Schlenk flask was filled with 1.03 g (3.00 mmol) 1 and 3 mL dry THF and the solution was deoxygenated for 20 min. Concurrently, a dry pear-shaped flask was filled with 1 mL DMSO and 180 mg (2.25 mmol) pyridine, and the solution was deoxygenated for 20 min. Then, 213 mg (1.00 mmol) DAHQ was added to the pear-shaped flask and allowed to dissolve. The Schlenk flask was kept under argon and filled with 31 mg (0.05 mmol) ytterbium triflate Yb(OTf)<sub>3</sub>, and heated to 60°C. The DAHQ solution was added dropwise and 1 mL THF was added after 2 h; stirring continued at 60°C overnight. The warm mixture was diluted with a small volume of CHCl<sub>3</sub> to dissolve the solids and the mixture was precipitated in 150 mL methanol at  $-78^{\circ}$ C. The precipitate was filtered and rinsed with methanol to yield a white powder (300 mg, 55 %), mp 102–104°C.  $\delta_{\rm H}$ (CDCl<sub>3</sub>) 7.81 (s, 2H), 7.46 (d, J 8, 2H), 7.02 (d, J 4, 2H), 3.15 (d, J 8, 4H), 1.75 (m, 2H), 1.39–1.29 (comp, 16H), 0.93 (t, J 8, 6H), 0.86–0.95 (comp, 12H). δ<sub>C</sub> (CDCl<sub>3</sub>) 160.9, 148.2, 140.1, 131.9, 128.9, 123.9, 100.5, 40.9, 34.2, 33.0, 29.0, 26.1, 23.2, 14.3, 11.1. m/z 549.2604. HRMS (ESI) Anal. Calc. for C<sub>32</sub>H<sub>41</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> 549.2604. Found 549.2602.

### 2,6-Bis(3-(2-ethylhexyl)-5-bromothien-2-yl)benzo[1,2d:4,5-d']bisoxazole (**3**)

A small flask, protected from light, was filled with 560 mg (1.02 mmol) **2** and dissolved in 35 mL CHCl<sub>3</sub>/acetic acid (6 : 1). Upon warming the solution to 40°C, 540 mg (3.06 mmol) N-bromosuccinimide (NBS) was added portion-wise followed by two drops of HBr. The reaction was stirred for three days at 40°C, then poured in 300 mL cold methanol. The precipitate was filtered, rinsed with methanol, and the crude product was recrystallised from ethyl acetate to yield yellow crystals (500 mg, 69%), mp 157–159°C.  $\delta_{\rm H}$  (CDCl<sub>3</sub>)  $\delta$  (d, *J* 8, 2H), 6.98 (s, 2H), 3.10 (d, *J* 8, 4H), 1.71 (m, 2H), 1.31–1.37 (comp, 16H), 0.92 (t, *J* 8, 6H), 0.89 (t, *J* 8, 6H).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 159.7, 148.1, 147.7, 140.1, 135.6, 125.4, 117.0, 100.6, 40.8, 34.2, 32.9, 29.0,

# 26.0, 23.2, 14.3, 11.0. *m/z* 707.0794. HRMS (ESI) Anal. Calc. for C<sub>32</sub>H<sub>39</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> 707.0794. Found 707.0798.

### 4,8-Dibromo-2,6-bis(3-(2-ethylhexyl)thien-2-yl)benzo [1,2-d:4,5-d']bisoxazole (**4**)

A dry Schlenk flask was filled with 3.95 g (11.5 mmol) 1, 4 mL dry THF, and 4 mL dry N,N-dimethylacetamide (DMA), and the solution was deoxygenated for 20 min. The solution was warmed to 55°C under argon and 119 mg (0.19 mmol) Yb(OTf)<sub>3</sub> was added. Then, 1.15 g (3.85 mmol) of freshly prepared Br-DAHQ was added portion-wise over 20 min followed by 3 mL THF after 2 h. Stirring was continued at 55°C overnight and the warm mixture was poured in 200 mL cold methanol. The precipitate was filtered, rinsed with methanol, and the crude product was recrystallised from ethyl acetate to yield off-white crystals (485 mg, 19%), mp 205–207°C. δ<sub>H</sub> (CDCl<sub>3</sub>) 7.51 (d, J8, 2H), 7.03 (d, J4, 2H), 3.20 (d, J8, 4H), 1.79 (m, 2H), 1.43–1.29 (comp, 16H), 0.92 (t, J 8, 3H), 0.87 (t, J 8, 3H).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 161.0, 148.2, 146.5, 139.4, 132.1, 129.9, 122.9, 91.2, 40.7, 34.5, 32.6, 28.8, 25.7, 23.3, 14.3, 10.8. m/z 707.0794. HRMS (ESI) Anal. Calc. for C<sub>32</sub>H<sub>39</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> 707.0794. Found 707.0798.

### 4,8-Bis(3,5-di-(2-ethylhexyloxy)phenylethynyl)-2,6-bis (3-(2-ethylhexyl)thien-2-yl)benzo[1,2-d:4,5-d'] bisoxazole (**5**)

A dry two-neck round-bottom flask equipped with a reflux condenser was filled with 887 mg (2.48 mmol) 6, 1.5 mL (11.0 mmol) diisopropylamine (<sup>i</sup>Pr<sub>2</sub>NH), and 12 mL dry THF, and the solution was deoxygenated for 30 min. The flask was filled with 775 mg (1.10 mmol) 4, 10.5 mg (0.055 mmol) CuI, and 38.6 mg (0.055 mmol) bis(chloro)bis(triphenylphosphine) palladium(II) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, and the mixture was further deoxygenated for 10 min, and heated to reflux for 48 h. The mixture was allowed to cool to room temperature, filtered through a small pad of celite, rinsed with CH<sub>2</sub>Cl<sub>2</sub>, and concentrated under vacuum. The crude product was purified by column chromatography using hexane/CH<sub>2</sub>Cl<sub>2</sub> eluent at varying ratios from 90:10 to 70: 30 to yield a viscous red oil (1.26 g, 91 %).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 7.49 (d, J 8, 2H), 7.03 (d, J 4, 2H), 6.86 (d, J 4, 4H), 6.54 (s, 4H), 6.54 (t, J 4, 2H), 3.89 (d, J 8, 8H), 3.23 (dq, J<sub>d</sub> 44, J<sub>q</sub> 8, 4H), 1.75 (m, 6H), 1.54–1.15 (comp, 48H), 0.97–0.91 (comp, 30H), 0.77 (t, J 8, 6H).  $\delta_{C}$  (CDCl<sub>3</sub>) 161.1, 160.5, 148.4, 148.5, 140.7, 131.9, 129.4, 124.0, 123.5, 110.4, 103.5, 100.4, 98.2, 79.4, 70.9, 40.8, 39.6, 34.4, 32.5, 30.7, 29.3, 28.7, 26.1, 24.1, 23.2, 23.1, 14.3, 14.2, 11.3, 11.0. m/z 1261.8035. HRMS (ESI) Anal. Calc. for C<sub>80</sub>H<sub>113</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub> 1261.8035. Found 1261.8024.

#### 3,5-Di-(2-ethylhexyloxy)ethynylbenzene (6)

In a round-bottom flask, 10.8 g (41.0 mmol) triphenylphosphine (PPh<sub>3</sub>) was dissolved in 30 mL CH<sub>2</sub>Cl<sub>2</sub>, cooled to 0°C, and 6.80 g (20.5 mmol) CBr<sub>4</sub> was added to the solution. Then, 3.63 g (10.0 mmol) 1,3-di-(2-ethylhexyloxy)benzaldehyde was dissolved in 20 mL CH<sub>2</sub>Cl<sub>2</sub> and the resulting solution was added drop-wise with a funnel to the reaction mixture. The reaction was stirred for 1 h at 0°C and then warmed to room temperature over 2 h. The solid was filtered, rinsed with hexane, and the filtrate was concentrated under vacuum. The crude mixture was suspended in hexane, loaded on a pad of silica gel, and the product was eluted with hexane. The eluted product was concentrated and dried under vacuum with stirring. The flask was back-filled with argon, and the resulting oil was dissolved in 40 mL dry THF, then cooled to  $-78^{\circ}$ C in a dry ice/acetone bath. Then, 10.3 mL n-butyl lithium ("BuLi; 2.5 M hexane solution) was added dropwise and the reaction was allowed to warm to room temperature overnight. The reaction was quenched with saturated NH<sub>4</sub>Cl (aq.) and extracted with hexane. The combined organic layers were washed with H<sub>2</sub>O and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was filtered and concentrated under vacuum. The product was purified by column chromatography using hexane as eluent to yield a yellow oil (2.90 g, 81 %).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 6.63 (s, 2H), 6.47 (s, 1H), 3.80 (d, *J* 8, 4H), 3.01 (s, 1H), 1.70 (m, 2H), 1.52–1.31 (comp, 16H), 0.93–0.89 (comp, 12H).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 160.4, 123.2, 110.4, 103.3, 84.0, 78.5, 39.5, 30.6, 29.2, 24.0, 23.2, 14.2, 11.2. *m/z* 359.2945. HRMS (ESI) Anal. Calc. for C<sub>24</sub>H<sub>39</sub>O<sub>2</sub> 359.2945. Found 359.2948.

### 4,8-Bis(3,5-di-(2-ethylhexyloxy)phenylethynyl)-2,6-bis (5-bromo-3-(2-ethylhexyl)thien-2-yl)benzo[1,2-d:4,5d']bisoxazole (**7**)

In a dry Schlenk flask, 1.02 g (0.81 mmol) 5 was dissolved in 20 mL dry THF and the solution was cooled to  $-78^{\circ}$ C in a dry ice/acetone bath. Then, 1.0 mL "BuLi (2.5 M hexane) was added dropwise over 10 min and stirred for 90 min at  $-78^{\circ}$ C. Then, 940 mg (2.84 mmol) CBr<sub>4</sub> was introduced and the reaction was stirred for 3 h at  $-78^{\circ}$ C and allowed to warm to room temperature overnight. The reaction was diluted with Et<sub>2</sub>O, quenched with saturated NH<sub>4</sub>Cl (aq.), and the layers were separated. The aqueous layer was extracted with Et<sub>2</sub>O, and the combined organic layers were washed with H2O and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was filtered and concentrated under vacuum, and the product was purified by column chromatography using hexane/CH<sub>2</sub>Cl<sub>2</sub> eluent at varying ratios from 95:5 to 70 : 30 to yield a sticky red oil (0.71 g, 62 %).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 7.00 (s, 2H), 6.84 (d, J4, 2H), 6.54 (t, J4, 4H), 3.89 (d, J8, 8H), 3.18 (dq,  $J_{d}$  40,  $J_{a}$  8, 4H), 1.75 (comp, 6H), 1.55–1.17 (comp, 48H), 0.97– 0.91 (comp, 30H), 0.78 (t, J 8, 6H). δ<sub>C</sub> (CDCl<sub>3</sub>) 160.5, 148.5, 148.3, 140.6, 134.6, 125.0, 123.8, 117.6, 110.4, 103.6, 100.7, 98.3, 79.1, 70.9, 40.8, 39.6, 34.5, 32.5, 30.7, 29.3, 28.7, 26.0, 24.1, 23.2, 23.1, 14.3, 14.26, 14.17, 11.3, 10.9. *m*/*z* 1417.6245. HRMS (ESI) Anal. Calc. for C<sub>80</sub>H<sub>111</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub> 1417.6245. Found 1417.6204.

### *4,8-Bis(3,5-di-(2-ethylhexyloxy)phenylethynyl)benzo* [1,2-b:4,5-b']dithiophene (**9**)

A dry two-neck round-bottom flask equipped with a reflux condenser was filled with 700 mg (1.95 mmol) 6 and 5.5 mL dry THF. The flask was cooled to 0°C and 0.82 mL "BuLi (2.5 M hexane) was added dropwise. The reaction was stirred at 0°C for 1 h, warmed to room temperature, and 187 mg (0.85 mmol) benzo[1,2-b:4,5-b']dithiophene-4,8-dione was introduced. The reaction was heated to reflux for 18 h and then allowed to cool to room temperature. A solution of 770 mg (3.40 mmol)  $SnCl_2 \cdot 2H_2O$  dissolved in 3.4 mL HCl (3 M) was added to the reaction mixture followed by addition of 5 mL THF. The resulting mixture was heated to reflux for 6 h and then allowed to cool to room temperature. The mixture was extracted with Et<sub>2</sub>O and the combined organic layers were washed with H<sub>2</sub>O and brine, and dried over Na2SO4. The solution was filtered and concentrated under vacuum. The crude product was purified by column chromatography (basic alumina) using hexane/CH<sub>2</sub>Cl<sub>2</sub> eluent at varying concentration ratios from 95:5 to 75:25 to yield a viscous yellow oil (380 mg, 49 %).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 7.73 (d, J 4, 2H), 7.60 (d, J 4, 2H), 6.82 (s, 4H), 6.53 (s, 2H), 3.90 (d, J 8,

8H), 1.75 (m, 4H), 1.56–1.34 (comp, 32H), 0.98–0.93 (comp, 24H).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 160.6, 140.5, 138.5, 128.3, 124.0, 123.4, 112.1, 110.1, 103.2, 99.6, 85.1, 70.8, 39.6, 30.7, 29.3, 24.1, 23.2, 14.3, 11.3. *m/z* 903.5414. HRMS (ESI) Anal. Calc. for C<sub>58</sub>H<sub>78</sub>O<sub>4</sub>S<sub>2</sub> 903.5414. Found 903.5404.

### 2,6-Bis(trimethylstannyl)-4,8-bis(3,5-di-(2ethylhexyloxy)phenylethynyl)benzo[1,2-b:4,5-b'] dithiophene (**11**)

In a dry Schlenk flask, 1.41 g (1.56 mmol) 9 was dissolved in 40 mL dry THF and the solution was cooled to  $-78^{\circ}$ C in a dry ice/acetone bath. Then, 1.75 mL "BuLi (2.5 M hexane) was added dropwise and the reaction was stirred for 90 min at -78°C. Then, 4.5 mL of trimethyltin chloride (1.0 M in THF) was added and the reaction allowed to warm to room temperature overnight. The reaction mixture was diluted in hexane, quenched with H<sub>2</sub>O, and the layers were separated. The organic layer was washed with H<sub>2</sub>O and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was filtered and concentrated under vacuum, and the crude product was dissolved in a minimal volume of warm CHCl<sub>3</sub>. The solution was precipitated in 400 mL cold methanol and the precipitate was filtered and rinsed with methanol to yield a yellow powder (1.64 g, 86 %), mp 101–103°C.  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 7.73 (s, 2H), 6.84 (d, J4, 4H), 6.53 (d, J4, 2H), 3.90 (d, J8, 8H), 1.75 (m, 4H), 1.57–1.34 (comp, 32H), 0.97–0.90 (comp, 24H), 0.49 (s, 18H). δ<sub>C</sub> (CDCl<sub>3</sub>) 160.5, 144.8, 143.7, 139.3, 131.0, 124.3, 110.23, 110.20, 103.1, 98.9, 85.8, 70.9, 39.6, 30.7, 29.3, 24.1, 23.2, 14.3, 11.3, -8.1. *m/z* 1231.4710. HRMS (ESI) Anal. Calc. for C<sub>64</sub>H<sub>95</sub>O<sub>4</sub>S<sub>2</sub>Sn<sub>2</sub> 1231.4710. Found 1231.4698.

### Synthesis of Polymers P1-P4

A dry two-neck flask equipped with a reflux condenser under argon was filled with stannane 3 or 7 and bromide 10 or 11 in equimolar amounts (outlined below). A solution of dry toluene and DMF (8:1) was then added and the mixture was thoroughly deoxygenated for 30 min. Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol-%) was introduced and the mixture was deoxygenated for an additional 10 min and heated to reflux for 48 h. One drop of trimethyl(phenyl)tin and 1 mL toluene were then added and reflux was continued for 6 h. Two drops of iodobenzene were added, followed by refluxing for 12h to complete the polymer end-capping process. The warm polymer solution was precipitated in methanol and filtered through a cellulose thimble. The polymer was placed in a Soxhlet extractor and washed with methanol, acetone, hexane, and CHCl<sub>3</sub>. The solution of polymer in chloroform was cooled to 50°C, stirred with Silicycle DMT® for 8 h to remove metal impurities, and the crude polymer was concentrated to  $\sim 5 \,\text{mL}$ under vacuum. The crude polymer solution was filtered through a small pad of silica gel using CHCl3 eluent and the solution was concentrated to  $\sim 5 \text{ mL}$  under vacuum. The polymer solution was re-precipitated in cold methanol, and the solid was filtered, rinsed with methanol, and dried under vacuum to yield polymers P1–P4.

Poly[(4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b'] dithiophene)-2,6-diyl-alt-(2,6-bis((2-ethylhexyl)thien-2yl)benzo[1,2-d:4,5-d']bisoxazole)] (**P1**)

**P1** was synthesised from 177 mg (0.25 mmol) **3** and 193 mg (0.25 mmol) **10** to yield an orange–red powder (107 mg, 43 %).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 7.52–7.33 (4H), 7.25 (2H), 6.83 (2H), 4.17 (4H), 3.16–3.05 (4H), 1.73–1.10 (60H).

Poly[(4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b'] dithiophene)-2,6-diyl-alt-(4,8-bis(3,5-di-(2ethylhexyloxy)phenylethynyl)-2,6-bis((2-ethylhexyl) thien-2-yl)benzo[1,2-d:4,5-d']bisoxazole)] (**P2**)

**P2** was synthesised from 276 mg (0.20 mmol) 7 and 150.3 mg (0.20 mmol) **10** to yield a dark red solid (146 mg, 44%).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 7.67 (2H), 6.97–6.90 (8H), 6.57 (4H), 4.25 (4H), 3.91 (8H), 3.26 (4H), 1.78–0.82 (120H).

### Poly[(4,8-bis-(3,5-di-(2-ethylhexyloxy)phenylethynyl) benzo[1,2-b:4,5-b']dithiophene)-2,6-diyl-alt)-(2,6-bis ((2-ethylhexyl)thien-2-yl)benzo[1,2-d:4,5-d'] bisoxazole)] (**P3**)

**P3** was synthesised from 177 mg (0.25 mmol) **3** and 307 mg (0.25 mmol) **11** to yield a dark red solid (289 mg, 80%).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 7.82 (2H), 7.38 (2H), 7.00 (2H), 6.90 (4H), 6.65 (2H), 4.04 (8H), 3.19 (2H), 1.83–0.97 (90H).

Poly[(4,8-bis(3,5-di(2-ethylhexyloxy)phenylethynyl) benzo[1,2-b:4,5-b']dithiophene)-2,6-diyl-alt-(4,8-bis (3,5-di-(2-ethylhexyloxy)phenylethynyl)-2,6-bis ((2-ethylhexyl)thien-2-yl)benzo[1,2-d:4,5-d'] bisoxazole)] (**P4**)

**P4** was synthesised from 240 mg (0.17 mmol) **7** and 207 mg (0.17 mmol) **11** to yield a red solid (252 mg, 69 %).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 7.87 (2H), 7.35 (2H), 6.87 (8H), 6.53 (d, *J* 8, 4H), 3.90 (q, *J* 8, 16H), 3.23–3.33 (4H), 1.87 (2H), 1.72 (8H), 1.52–1.21 (80H), 0.97–0.79 (60H).

### Computational Details

All computations were performed using *Gaussian 09* through the National Science Foundation Extreme Science and Engineering Discovery Environment and San Diego Supercomputer Center Trestles Cluster. Excited states were generated through time-dependent density functional theory and applied to the optimised ground state of each polymer subunits, n = 1, 2, 3, and 4. The long chain limits for the HOMO, LUMO, and band gap were generated from the excited computations and fitted using the Kuhn expression.<sup>[30]</sup>

### **Supplementary Material**

NMR spectra for all new compounds, thermal data, additional UV-Vis absorption and emission spectra for the polymers are available on the Journal's website.

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