Synthesis, Characterization, and OFET and OLED Properties of π -Extended Ladder-Type Heteroacenes Based on Indolodibenzothiophene

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Ladder-type heteroacenes based on indolodibenzothiophene have been synthesized. The route involved a regioselective twofold intramolecular acid-induced cyclization of the central bis(butylsulfinyl)phenyl unit onto the adjacent carbazole units, followed by dealkylation to give diindolobenzobisbenzothiophene (DIBBBT) derivatives. Importantly, this sequence proceeded efficiently in the presence of the chloro substituents which provided reactive sites for further π -extension of the DIBBBT core. The chloro derivative underwent twofold palladium-catalyzed Suzuki–Miyaura reactions with phenylboronic acid or 4-*n*-octylphenylboronic acid. Compounds have been characterized by ¹H NMR spectroscopy, mass spectrometry, elemental analysis, optical spectroscopy, and solution electrochemical studies. Organic field-effect transistors (OFETs) have been constructed based on drop-cast thin films and the performances as p-type semiconductor are presented. The chloro derivative was also copolymerized with 9,9-dioctyl-2,7-fluorenyl-enediboronic acid bis(1,3-propanediol) ester to give the alternating copolymer which exhibits blue photoluminescence in a solution processed organic light-emitting diode (OLED).

Conjugated oligomers are of particular interest in organic electronic and optoelectronic applications, for example as components for organic light-emitting devices (OLEDs),¹ solar cells,² and organic field-effect transistors (OFETs).³ The planar and rigid frameworks of ladder-conjugated oligomers facilitate electron delocalization compared to linear and branched counterparts and ladder systems generally show enhanced mechanical, thermal, and chemical stability. Classical systems with high charge carrier mobility are linear acenes (notably pentacene)⁴ although their oxidative stability is rather limited due to their narrow band gaps. Instability remains a significant issue with higher homologues.⁵ Pentacene also suffers from extreme insolubility, so derivatives with pendant functionality,⁶ and thiophene units in the backbone⁷ have been developed.

New ladder-type heteroacenes with multi-heteroatom components to enhance stability and alkyl substituents for improved solubility are current targets. Examples include fused oligothiophene,⁸ benzothiophenes,⁹ benzobisthiazole,¹⁰ thiazolothiazole,¹¹ indolocarbazole,¹² bisindenocarbazole,¹³ and thienopyrrole derivatives.¹⁴ In this regard, pyrrole, indole, and carbazole are attractive building blocks due to the ease of attaching solubilizing chains to the nitrogen atoms. Alkyl substituents attached to these sp² hybridized nitrogen atoms may align within the molecular planes and improve the intermolecular π - π stacking in the solid state. However, only a limited number of extended heteroacenes (>7 fused rings) have been synthesized,¹⁵ for example, diindolobenzobisbenzothiophene (DIBBBT) with 9 fused rings,^{9c} and they are

challenging target molecules. Extended linearly-condensed systems can offer enhanced π - π overlap in the solid state leading to high mobility.

We now describe the synthesis and characterization of new DIBBBT derivatives, in particular the first derivative **8** bearing functionality which has enabled subsequent transformations. The terminal chloro substituents of **8** have been utilized in palladium-catalyzed cross-coupling reactions to afford the diphenyl derivative **9**, the 4-*n*-octylphenyl derivative **10**, and the alternating copolymer **11**. The performances of OFETs based on drop-cast thin films of **8–10** as p-type semiconductors are presented, and OLEDs based on spin-coated thin films of **11** are described.

Results and Discussion

Synthesis. The synthetic strategy is outlined in Scheme 1. The significant new feature in our synthesis, compared to the previous synthesis of the DIBBBT skeleton,^{9c} is that we retained the 7-chloro substituent of 1 until the end of the sequence, where it provides a versatile handle for the attachment of terminal groups and π -extension by metal-catalyzed processes. Carbazole derivative 1 was synthesized by treatment of 4-bromo-4'-chloro-2-nitrobiphenyl with triethylphosphite at reflux, as described.¹⁶ Attachment of the 2-ethylhexyl substituent to 1 enhanced the solubility in organic solvents. Compound 2 was readily obtained and converted into the boronic ester derivative 3 by reaction with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, utilizing the enhanced reactivity of the bromo substituent in this reaction. A double



Scheme 1. Synthesis of DIBBBT derivatives 9 and 10 and polymer (DIBBBT-Fl)_n (11). Reagents and conditions: (i) Kt-OBu, THF, rt, then 2-ethylhexyl bromide, 60 °C (88%); (ii) *n*-BuLi, -78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, -78 °C (69%); (iii) [Pd(PPh₃)₂Cl₂], KOH, PhMe, THF, H₂O, reflux (59%); (iv) mcpba, DCM, 0 °C (90%); (v) MeSO₃H, rt (product 7 not purified); (vi) pyridine, reflux (30% from 6); (vii) K₃PO₄•2H₂O, phenylboronic acid or 4-*n*-octylphenylboronic acid (excess), THF, water, Pd(OAc)₂, dicyclohexyl-2',6'-dimethoxy-2-biphenylylphosphine (Sphos), 60 °C (87% or 90%); (viii) (a) K₃PO₄•2H₂O, 12 (1.0 equiv), THF, water, Pd(OAc)₂, Sphos, 60 °C, (b) 4-*n*-butylbromobenzene, 60 °C (c) 4-*n*-butylphenylboronic acid 60 °C (82%).

reaction of **3** with reagent **4** under standard Suzuki–Miyaura cross-coupling conditions gave **5** in 59% yield. Oxidation of **5** with *m*-chloroperoxybenzoic acid gave disulfinyl derivative **6**. The ¹H NMR spectrum of **6** (See Supporting Information) is consistent with two diastereomers arising from the presence of two sulfoxide groups in the molecule. Reaction of **6** with methanesulfonic acid gave a yellow solid product, presumed to be the intermediate salt **7**, based on literature precedents.⁹ Salt **7** was isolated but not purified; it was used directly in the next

step. Dealkylation of 7 was achieved in refluxing pyridine⁹ to afford 8 (30% yield from 6). The ¹HNMR spectrum of 8 confirmed a highly symmetric structure with the regiochemistry shown, with no evidence obtained for the formation of isomeric products. It was gratifying that the chloro substituents were retained throughout the reaction conditions; this was crucial for our strategy of retaining reactive terminal sites for further functionalization. Compound 8 served as an efficient synthon for compounds with extended conjugation, namely diphenyl

derivatives 9 and 10 and the alternating copolymer 11. Twofold Suzuki-Miyaura reactions of 8 with phenylboronic acid or 4-n-octylphenylboronic acid using a mixture of palladium acetate and dicyclohexyl-2',6'-dimethoxy-2-biphenylylphosphine (Sphos) as catalyst¹⁷ gave products 9 and 10 in 87 and 90% yields, respectively. Compounds 8-10 were isolated as air-stable yellow solids with limited solubility in common organic solvents. Using similar conditions, compound 8 was copolymerised¹⁸ with 9,9-dioctyl-2,7-fluorenylenediboronic acid bis(1,3-propanediol) ester 12^{19} to afford an alternating copolymer which was end-capped in situ with 4-*n*-butylphenyl groups. This was achieved by sequential reaction with 4-nbutylbromobenzene and 4-n-butylphenylboronic acid to yield the (DIBBBT-Fl)_n copolymer 11 which was obtained in 82%vield as a pale vellow solid. Copolymer 11 had $M_{\rm w}$ 48 kDa. polydispersity of ca. 1.8 and showed good thermal stability with $T_d^{5\%}$ 380 °C, typical for conjugated polycarbazole²⁰ and polyfluorene²¹ derivatives.

UV-vis Absorption, Photoluminescence Spectra, and Solution Electrochemical Properties. Absorption and emission spectra of compounds 8 and 9 were recorded in chloroform (Figure 1). The strong absorption bands at 367 and 389 (8) and 378, 389, and 398 nm (9) are attributed to π - π * transitions of the heteroacene backbone. A small red shift (ca. 10 nm) in both the absorption and emission spectra is observed on replacing the terminal chlorine substituents of 8 with phenyl rings (compound 9) consistent with extended conjugation in 9. Based on the onset of the low energy band (ca. 440 nm), the optical band gap of 9 can be estimated as 2.82 eV. Both compounds show blue fluorescence (λ_{max} 437,



Figure 1. Absorption and emission spectra of 8 and 9 in chloroform.

464 for **8**, and 443, 472 nm for **9**). Photoluminescence quantum yields in CHCl₃ (Φ : 5.1% for **8** and 7.9% for **9**) were determined by using 9,10-diphenylanthracene (λ_{ex} 366 nm, Φ 0.81 in EtOH) as standard. Octyl-substituted compound **10** afforded similar absorption and emission maxima compared with **9** (see Experimental section). Copolymer **11** is a blue emitter: compared to **9**, the absorption and photoluminescence spectra of **11** (Figure S1) are slightly broadened and red shifted by ca. 15 nm: for **11** λ_{max} (em) (CHCl₃) 459, 472 (sh) nm. Photoluminescence quantum yields of **11** were 63 (±5)% in toluene and 21 (±5)% in film. For film the data was obtained by using an integrating sphere.²² These data are typical for fluorene copolymers.²¹

The redox potentials of **8** and **9** were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in acetonitrile. The CVs of **8** and **9** revealed reversible oxidation waves at $E^{1/2}$ 0.989 V (E^{ox} 1.023; E^{red} 0.956 V) and 0.956 V (E^{ox} 0.989; E^{red} 0.922 V) vs. Ag/Ag⁺, respectively, when the scan was terminated at +1.1 V (potentials calibrated with ferrocene as the internal standard) (Figure 2a). Since octyl-substituted compound **10** did not dissolve in acetonitrile, a CV of **10** was measured in dichloromethane and revealed a reversible wave at $E^{1/2}$ 0.954 V (E^{ox} 0.994; E^{red} 0.914 V) and two additional quasi-reversible oxidation waves as shown in Figure 2b.

The DPVs of **8** and **9**, vs. ferrocene/ferrocenium⁺ are shown in Figure 3. Both compounds show three clear oxidation peaks each of which is shifted to less positive potentials when the chloro substituents are replaced by phenyl (i.e., **8** \rightarrow **9**). Taking the HOMO level of ferrocene as -4.8 eV,²³ the HOMO levels of **8** and **9** can thus be estimated as -5.3 eV based on the onset of the first oxidation wave ($E_{\text{ox}}^{\text{onset}}$ ca. +0.50 and ca. 0.47 V). This value is lower than that of pentacene (-4.60 eV)²⁴ indicating enhanced oxidative stability of **8** and **9**, and is similar to that of indolo[3,2-*b*]carbazole derivatives -(5.4-5.6 eV) reported by Leclerc et al.^{12e}

Organic Field-Effect Transistor Devices. Device properties have not been reported previously for the DIBBBT system. To investigate the carrier transporting properties, preliminary FET devices were tested by using simple DIBBBT derivatives **8–10** with chloro, phenyl, and alkylphenyl groups. The FET devices were fabricated on thermally oxidized silicon dioxide with interdigitated Au bottom electrodes. The surface of silicon dioxide was treated with hexamethyldisilazane (HMDS). Thin films were deposited by a drop-cast method from the chloroform solution followed by annealing at 110–180 °C for 20 min



Figure 2. Cyclic voltammograms of (a) 8 (dotted line) and 9 (solid line) in acetonitrile solution and (b) 10 in dichloromethane.



Figure 3. DPVs of compounds (a) 8 and (b) 9 in acetonitrile solution, vs. Fc/Fc⁺.

in a high vacuum chamber (ca. 10^{-5} Pa). The FET measurements were carried out in situ and in the air. All films of **8–10** exhibited p-type FET characteristics (Table 1). Among them, compound **9** with terminal phenyl groups afforded the highest mobility of 1.2×10^{-2} cm² V⁻¹ s⁻¹ on HMDS treated surface as shown in Figure 4. Film **9** on untreated surface showed notable air stability as expected from the oxidation potential (Table 1). On the other hand, compound **10** with octyl groups did not improve the carrier transportation, although the surfaces of films were apparently flat and continuous. In this system, alkyl groups of the molecular long axis may disturb the formation of large overlap between molecular orbitals. However, suitable elongation and modification to the DIBBBT core is expected to increase the carrier transporting properties.

The X-ray diffraction profiles of drop-cast films of **8** and **9** indicate a primary diffraction peak at $2\theta = 4.5$ (*d*-spacing 1.97 nm) and 5.2° (*d*-spacing 1.69 nm), respectively (Figure 5). Although crystal structures could not be obtained, the XRD profiles suggest that the molecules are oriented with a specific regularity on the substrate surface. Compound **8** with terminal chloro substituents showed a longer *d*-spacing than compound **9**, although the calculated molecular length of **8** (2.26 nm) is shorter than that of **9** (2.98 nm). On the other hand, the film of **8** showed lower mobility than that of **9**. Compound **8** afforded a discontinuous crystalline film compared with **9**, and the terminal chloro substituents may be unfavorable for the hole transportation.

Polymer Light-Emitting Diode (PLED) Devices of 11. A copolymer **11** containing DIBBBT cores was used for fabrication of polymer LEDs, and two device structures were

Comp.	Surface of SiO ₂	Measurement condition	Hole mobility $/cm^2 V^{-1} s^{-1}$	On/off ratio	Threshold /V
8	Untreated	In vacuo	5.6×10^{-6}	1×10^{3}	-15
9	Untreated	In vacuo	4.0×10^{-3}	1×10^{6}	-39
	Untreated	In the air, after 12 h	6.3×10^{-4}	5×10^{5}	-10
	Untreated	In the air, after 24 h	7.2×10^{-4}	5×10^{5}	-5
	HMDS	In vacuo	1.2×10^{-2}	2×10^{4}	-11
10	Untreated	In vacuo	4.1×10^{-5}	3×10^{3}	-42
	HMDS	In vacuo	6.3×10^{-4}	1×10^{5}	-25

 Table 1. FET Characteristics^{a)} of Compounds 8–10

a) Bottom contact geometry. Interdigitated gold source and drain electrodes.



Figure 4. (a) Output and (b) transfer characteristics of FET based on 9 (HMDS treated surface).



Figure 5. X-ray diffraction profiles of films based on (a) 8 and (b) 9. Calculated molecular lengths (MOPAC: PM5 method).

tested. Solution processing was used for deposition of the emissive layer. Devices A were fabricated with the configuration ITO/PEDOT:PSS/**11**/Ba/Al. To achieve more balanced electron injection and transport,^{25,26} a second set of devices (devices B) were fabricated with addition of the electron transporter 2-(4-biphenylyl)-5-(*t*-butylphenyl)-1,3,4-oxadiazole (PBD) blended into the emissive layer. Following previous procedures,²⁶ screening of various concentrations of PBD (5–50% w/w) showed that 30% w/w incorporation was optimal. Device B architecture is, therefore: ITO/PEDOT: PSS/**11**:PBD (30% w/w)/Ba/Al.

The characterization of the devices is shown in Figures 6-8. The electroluminescence spectra of devices A and B were identical showing that emission is solely from polymer 11, λ_{max} 484, 510 (shoulder) visible as blue-green light (Figure 6). Figure 7 shows the external quantum efficiency (EQE), the device current efficiency, and brightness data for devices A and B. Device B, with the added electron transport material, exhibits significantly improved performance. This can be explained by the predominant hole transport characteristics of the DIBBBT core of the polymer limiting the efficiency of devices A. Devices B achieve respectable values for EQE (0.9%) current efficiency $(2.7 \text{ cd } \text{A}^{-1})$ and brightness (1500 cd m^{-2}) at a current density of 60 mA cm^{-2} . Brightness increases to ca. 3000 cd m⁻² at higher current densities. The current-voltage (I-V) characteristics are shown in Figure 8. Turn-on voltages for light emission are low (3.0-3.5 V). The



Figure 6. Electroluminescence spectrum of device B: ITO/PEDOT:PSS/11:PBD (30% w/w)/Ba/Al at current density of 20 mA cm⁻².



Figure 7. (a) EQE, (b) efficiency, and (c) brightness data for the device A (squares) and the device B (circles).

enhanced performance of the blended device B is again evident in these data. It should be noted that these are simple solution processed single-active-layer devices. These are unoptimized devices and performance might be improved by inserting



Figure 8. Current–voltage data for the device A (squares) and the device B (circles).

additional layers to improve charge balance. However, we have not explored this aspect as our aim is to retain as simple a device structure as possible.

Conclusion

We have described the efficient synthesis of the extended ladder-type heteroacene 8 bearing nine linearly-fused rings and terminal chloro substituents which have been efficiently converted into phenyl and octylphenyl groups by a palladiumcatalyzed cross-coupling reaction to afford 9 and 10. Compounds 8-10 are blue emitters; a red shift (ca. 10 nm) in both the absorption and emission spectra is observed for 9 compared to 8. These compounds show multistage oxidation processes in solution electrochemical studies. Films 8-10 prepared by the drop-casting method exhibited p-type FET characteristics with mobilities of 10^{-6} to 10^{-2} cm² V⁻¹ s⁻¹ (maximum $1.2 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) with high on/off ratio. FET device on 9 showed notable air stability. This work has demonstrated the potential of DIBBBT derivatives for organic electronic device applications. Furthermore, it has been established that 8 is a suitable building block for DIBBBT copolymers, as exemplified by the synthesis of the blueemitting (DIBBBT-Fl)_n copolymer 11.

Experimental

Compound 5. To the solution of **3** (0.727 g, 1.65 mmol) and 4 (0.320 g, 0.78 mmol) in toluene (50 mL) were added THF (5 mL) and water (5 mL), followed by KOH (0.21 g) and [Pd(PPh₃)₂Cl₂] (27 mg, 5 mol %). The mixture was refluxed with stirring for 12 h then evaporated under vacuum to dryness and the residue was chromatographed on a silica column (eluent: hexane-DCM 3:1 v/v). The product was recrystallized from DCM-ethanol to yield 5 as a white solid (0.40 g, 59%); mp 147.0–148.5 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.13 (d, J = 8.0 Hz, 2H), 8.02 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 0.8 Hz, 2H), 7.41–7.38 (m, 4H), 7.36 (dd, J = 1.4, 8.0 Hz, 2H), 7.22 (dd, J = 1.8, 8.3 Hz, 2H), 4.16 (d, J = 7.4 Hz, 4H), 2.81-2.75(m, 4H), 2.13 (m, 2H), 1.55 (m, 4H), 1.50–1.19 (m, 20H), 0.88 (m, 18H). ¹³C NMR (101 MHz, CDCl₃): δ 142.00, 141.96, 140.98, 138.02, 133.02, 131.49, 129.85, 121.72, 121.31, 121.14, 120.90, 119.92, 119.43, 110.43, 109.14, 47.78, 39.32, 33.14, 31.02, 30.76, 28.77, 24.42, 23.07, 21.98, 14.01, 13.60,

10.97. Anal. Calcd for $C_{54}H_{66}Cl_2N_2S_2$: C, 73.86; H, 7.58; N, 3.19%. Found: C, 73.93; H, 7.58; N, 3.15%. MS (MALDI-TOF): m/z 876.2 (M⁺, 100%).

Compound 6. To a solution of 5 (395 mg, 0.45 mmol) in DCM (50 mL) at 0 °C was added a solution of m-chloroperoxybenzoic acid (250 mg, Avocado, 57-86%) in DCM (15 mL) dropwise through a syringe. The mixture was stirred with ice-bath cooling for 12 h to yield a colorless clear solution, which was concentrated and chromatographed on a silica column (eluent: 3% diethyl ether in DCM) to afford a white foamy solid (368 mg, 90%) as mixtures of two diastereomers arising from the presence of two sulfoxide groups, mp 93.0-94.5 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.18 (s, 2H), 8.14 (d, J = 8.1 Hz, 2H), 8.03 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 3.0 Hz, 2H. major 65%), 7.50 (br s. 2H. minor 35%), 7.41 (d. J =1.5 Hz, 2H), 7.36 (br d, J = 8.1 Hz, 2H, major 65%), 7.31 (br d, J = 8.1 Hz, 2H, minor 35%), 7.22 (dd, J = 1.5, 8.4 Hz, 2H), 4.18 (d, J = 7.5 Hz, 4H), 2.65–2.31 (m, 4H), 2.10 (br m, 2H), 1.68-1.11 (m, 24H), 1.05-0.79 (m, 12H), 0.63 (m, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 144.99, 141.98, 141.03, 140.07, 134.36, 132.06, 126.56, 122.55, 121.32, 120.94, 120.74, 120.29, 119.76, 109.49, 109.32, 53.56, 47.62, 39.25, 30.89, 28.73, 28.56, 24.31, 24.09, 22.97, 21.29, 13.95, 13.26, 10.99, 10.81. MS (MALDI-TOF): m/z 909.3 (M⁺, 100%). Anal. Calcd for C54H66Cl2N2O2S2: C, 71.26; H, 7.31; N, 3.08%. Found: C, 71.35; H, 7.35; N, 3.03%.

Compound 8. Compound 6 (0.41 g, 0.45 mmol) was mixed with methanesulfonic acid (5 mL) and the yellow solution was stirred at r.t. for 12 h to yield a greenish-yellow solution. Icewater (50 mL) was added with stirring and the precipitated vellow solid was collected by suction filtration and washed with a large volume of water, then dried in air. The solid (presumed to be 7) was dissolved in pyridine (30 mL) and the solution was refluxed for 3 h. The pyridine was removed by vacuum evaporation and the yellow solid residue was boiled in ethanol (25 mL) for 5 min then suction filtered. The precipitate was dissolved in chloroform then flash columned on silica (eluent: chloroform). The first fraction collected was recrystallized from chloroform-ethanol to afford 8 as yellow microcrystals (0.103 g, 30%); mp > 320 °C. ¹H NMR (500 MHz, 373 K, TCE- d_2): δ 8.54 (s, 2H), 8.46 (s, 2H), 8.05 (d, J =8.2 Hz, 2H), 7.99 (s, 2H), 7.35 (s, 2H), 7.27 (d, J = 8.1 Hz, 2H), 4.13 (s, 4H), 2.18 (s, 2H), 1.61-1.26 (m, 16H), 1.01 (t, J = 7.3 Hz, 6H), 0.95 (t, J = 7.1 Hz, 6H). MS (MALDI-TOF): m/z 760.3 (M⁺, 100%). Anal. Calcd for C₄₆H₄₆Cl₂N₂S₂: C, 72.51; H, 6.09; N, 3.68%. Found: C, 72.48; H, 6.10; N, 3.67%. UV-vis: λ_{max} (CHCl₃) (log ε) 285 (4.99), 367 (5.01), 389 (5.04) nm.

Compound 9. All procedures were performed under argon. A mixture of palladium acetate (5.0 mg) and dicyclohexyl-2',6'-dimethoxy-2-biphenylylphosphine (Sphos) (20.0 mg) in degassed THF/water (6 mL, 3:1 v/v) was stirred for 10 min to generate the active catalyst. To a mixture of **8** (30 mg, 0.0394 mmol), $K_3PO_4 \cdot 2H_2O$ (100 mg, 0.403 mmol) and phenylboronic acid (45 mg, 0.369 mmol) was added a mixture of THF/water (12 mL, 3:1 v/v) and the temperature raised to 60 °C, whereupon the freshly-prepared catalyst solution (2 mL) was added. The mixture was stirred at 60 °C for 20 h, cooled to r.t., the solvent was removed and the residue was extracted with

DCM. The organic layer was washed with water, then with brine, dried (MgSO₄) and evaporated in vacuo. The residue was purified by column chromatography on silica (eluent: DCM) and recystallized from a mixture of DCM–ethanol to yield **9** (29 mg, 87%) as a pale yellow solid; mp >320 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.55 (s, 2H), 8.25 (d, J = 8.0 Hz, 2H), 8.14 (br s, 2H), 7.67 (dd, J = 7.8, 1.5 Hz, 4H), 7.56 (d, J = 7.7 Hz, 2H), 7.49–7.38 (m, 8H), 7.29 (br s, 2H), 3.43 (br d, 4H), 1.89 (m, 2H), 1.40–1.19 (m, 16H), 0.96–0.82 (m, 12H). MS (MALDI-TOF): m/z 844.3 (M⁺, 100%). Anal. Calcd for C₅₈H₅₆N₂S₂•0.5H₂O: C, 81.55; H, 6.73; N, 3.28%. Found: C, 81.36; H, 6.62; N, 3.05%. UV–vis: λ_{max} (CHCl₃) (log ε) 288 (4.92), 378 (5.03), 389 (5.03), 398 (5.06) nm.

Compound 10. All procedures were performed under argon. A mixture of palladium acetate (5.0 mg) and dicvclohexyl-2',6'-dimethoxy-2-biphenylylphosphine (Sphos) (20.0 mg) in degassed THF/water (6 mL, 3:1 v/v) was stirred for 10 min to generate the active catalyst. To a mixture of 8 (17 mg, 0.0224 mmol), $K_3PO_4 \cdot nH_2O$ (60 mg) and 4-*n*-octylphenylboronic acid (54 mg, 0.231 mmol) was added a mixture of THF/water (12 mL, 3:1 v/v) and the temperature raised to 60 °C, whereupon the freshly-prepared catalyst solution (2 mL) was added. The mixture was stirred at 60 °C for 21 h, cooled to r.t., the solvent was removed and the residue was extracted with DCM. The organic layer was washed with water, then with brine, dried (Na₂SO₄) and the organic layer evaporated in vacuo. The residue was purified by column chromatography on silica (eluent: DCM) and recystallized from a mixture of DCM-ethanol to vield 10 (21 mg, 90%) as a vellow solid; mp 309.5-315.5 °C (a sharp peak of DSC). ¹HNMR (300 MHz, CDCl₃): δ 8.51 (s, 2H), 8.21 (d, J = 8.4 Hz, 2H), 8.16 (s, 2H), 7.59 (d, J = 8.4 Hz, 4H), 7.53 (dd, J = 6.6, 1.5 Hz, 2H), 7.44 (s, 2H), 7.31 (br s, 2H), 7.24 (d, J = 8.4 Hz, 4H), 3.49 (br d, J = 6.6 Hz, 4H), 2.70 (t, J = 7.8 Hz, 4H), 1.95–1.85 (m, 2H), 1.80-1.60 (m, 4H), 1.50-1.10 (m, 36H), 0.95-0.80 (m, 18H). MS (FAB): m/z 1069 (M⁺). Anal. Calcd for C74H88N2S2: C, 83.09; H, 8.29; N, 2.62%. Found: C, 82.74; H, 8.41; N, 2.56%. UV-vis: λ_{max} (abs) (CHCl₃) (log ε) 287 (5.03), 387 (5.04), 400 (5.05) nm. λ_{max} (em) (CHCl₃) 444, 471 nm.

(DIBBBT-FI), 11. A mixture of DIBBBT-Cl₂ 8 (7.6 mg, 0.010 mmol) and 9,9-dioctyl-2,7-fluorenylenediboronic acid bis(1,3-propanediol) ester 12 (5.8 mg, 0.010 mmol), K₃PO₄. 2H₂O (10 mg, 0.040 mmol) was prepared in THF/water (12 mL, 3:1 v/v) and the temperature raised to 60 °C. Freshlyprepared catalyst solution (as described for compound 9) (2 mL) was added and the mixture was stirred at 60 °C for 20 h. 4-n-Butylbromobenzene (0.05 mL) was added and stirring continued at 60 °C for 1 h before 4-butylbenzeneboronic acid (10 mg) was added and stirring continued at 60 °C for 1 h. After cooling to r.t., the mixture was added slowly to stirring methanol (30 mL) to precipitate the crude polymer as a yellow solid. The solid was washed with methanol, water, and hexane. The resulting yellow solid was placed in a thimble and extracted in a Soxhlet apparatus with acetone for 20 h. After removal of the acetone from the thimble under vacuum, the residue was extracted into chloroform. The chloroform solution was concentrated under reduced pressure to ca. 5 mL and poured dropwise into methanol (10 mL) with vigorous stirring

to precipitate which was washed sequentially with methanol and hexane and dried in vacuo at room temperature to afford copolymer **11** as a pale yellow solid (9.0 mg, 82% yield). Size exclusion chromatography (SEC, vs. polystyrene standard): M_w 48 kDa, polydispersity of ca. 1.8; thermal decomposition $T_d^{5\%}$ 380 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.50–8.10 (m), 7.64– 7.34 (br), 3.42 (br), 2.13 (br), 1.43–1.20 (br), 0.98–0.80 (br). UV–vis: λ_{max} (abs) (CHCl₃) 327, 385, 412 nm; λ_{max} (em) (CHCl₃) 459, 472 (sh) nm.

OFET Fabrication. FET devices were prepared with bottom contact geometries. Highly doped n⁺-Si wafers were used as substrates, and a layer of 300 nm of silicon dioxide (grown by thermal oxidation) was used as a gate dielectric layer. Cr (10 nm)/Au (20 nm) were sequentially evaporated and photolithographically delineated to obtain source and drain electrodes. The interdigitated structure of the source-drain contacts determined a channel length of 25 µm and a channel width of 294 mm ($6 \text{ mm} \times 49$). Substrates were cleaned with acetone, 2-propanol and ozone for 20 min, and immersed in hexamethyldisilazane (HMDS) at rt for over 12 h to treat the surface. Thin films of compounds 8-10 were deposited by a drop-cast method of chloroform solution onto the channel region followed by annealing at 110-180 °C for 20 min in a high vacuum chamber (ca. 10^{-5} Pa). The FET measurements were carried out in situ then in air. Mobilities (μ) were calculated in the saturation regime by the relationship: $\mu_{\text{sat}} = (2I_{\text{DS}}L)/[WC_{\text{ox}}(V_{\text{G}} - V_{\text{th}})^2]$ where I_{DS} is the sourcedrain saturation current: C_{ox} is the oxide capacitance. V_{G} is the gate voltage and $V_{\rm th}$ is the threshold voltage. The latter can be estimated as the intercept of the linear section of the plot of $(I_{\rm DS})^{1/2}$ vs. $V_{\rm G}$.

OLED Fabrication. OLEDs were fabricated on indium tin oxide (ITO)-coated glass substrates of thickness 125 nm and possessing a sheet resistance of 20Ω /square. Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS), obtained commercially from Bayer A.G. Germany, was spin coated at 2500 rpm for 60 s to produce a ca. 45 nm thick hole-transporting layer (HTL). These HTLcoated substrates were then annealed at 200 °C for 5 min to remove any residual water. A chlorobenzene solution of 5 mg mL^{-1} of polymer 11 was prepared (Devices A). For Devices B 30% w/w of 2-(4-biphenylyl)-5-(t-butylphenyl)-1,3,4-oxadiazole (PBD) was added to the solution. The mixtures were filtered with a 0.45 µm pore filter and spin coated at 2500 rpm on the top of the HTL and baked for 10 min at 120 °C to produce film thicknesses of 50 ± 5 nm. The samples were then introduced into a nitrogen glove box, where barium cathodes (thickness ca. 4 nm) were evaporated onto the device at a rate of ca. 1 Å s^{-1} under vacuum at a pressure of ca. 1×10^{-6} mmHg. Subsequently a layer of aluminium (100 ± 5 nm) was deposited under the same conditions. All samples were encapsulated inside a glove box. The devices were tested on the same day as their preparation to minimize any degradation of the cathode.

The current–voltage (I-V) and the emission characteristics of the OLEDs were measured using a calibrated integrating sphere. The electroluminescence (EL) spectra were measured using an Ocean Optics USB 4000 CCD spectrometer supplied with 400 µm UV–vis fiber optics. J. Nishida thanks the Japan Society for the Promotion of Science (JSPS) for the International Training Program (Japan-Europe-U.S. International Training Program for Young Generation in Molecular Materials Science for Development of Molecular Devices). We thank EPSRC for funding the work in Durham. We thank A. P. Monkman for use of equipment for OLED characterization.

Supporting Information

Detailed experimental procedures; absorption and emission spectra of (DIBBBT-Fl)_n **11**; additional OFET data for **8–10**; copies of ¹H, ¹³C NMR, and mass spectra. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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