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Highly Fluorescent Dithieno[3,2-*b*:2′,3′-*d*]pyrrole-Based Materials: Synthesis, Characterization, and OLED Device Applications

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ABSTRACT: Dithieno[3,2-*b*:2′,3′-*d*]pyrrole-arylene copolymers have been prepared via Stille coupling to produce soluble, processable materials with good molecular weights. Solution and solid-state characterization of the copolymers is described, including photophysical and electrochemical studies, and these properties are compared to those of the parent poly(dithieno[3,2-*b*:2′,3′-*d*]pyrrole)s as well as analogous bithiophene-arylene copolymers. Poly(*N*-decyldithieno[3,2-*b*:2′,3′-*d*]pyrrole) and the newly generated copolymers were then used as emissive layers to fabricate initial LEDs, and the initial evaluation of their device performance is presented.

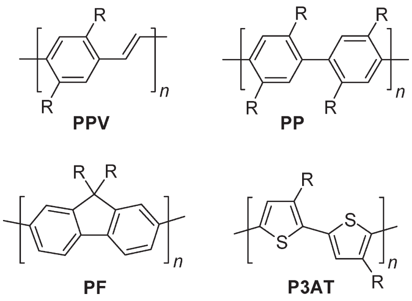
Introduction

Because conjugated organic polymers combine the electronic and optical properties of inorganic semiconductors with many of the desirable properties of organic plastics, including mechanical flexibility and low production costs, they have received considerable fundamental and technological interest over the last few decades.[1−3] Another key advantage of these materials is the ability to tune the electronic and optical properties on the molecular level via synthetic modification. The continued development of these materials has led to their current use in such applications as sensors, field-effect transistors (FETs), organic photovoltaic (OPV) devices, electrochromic devices, and light-emitting diodes (LEDs).[1−3]

Although inorganic LEDs have been commercially available since the early 1960s, the first conjugated polymer-based LEDs were produced at Cambridge in 1989 using poly(phenylene vinylene) (PPV, Chart 1).[4,5] This initial work then provided significant motivation for the development of new electroluminescent conjugated materials as active materials for LED and display applications.[4−7] Because of their environmental stability and ease of synthetic modification, polythiophenes are thought to be one of the most versatile classes of conjugated polymers and typically exhibit the greatest amount of synthetic diversity.[1−3,5] As a consequence, a wide variety of polythiophene-based materials have been produced and investigated for their photoluminescent properties[4−6] and a number of poly(3-alkylthiophene)s (P3ATs) have been studied as emissive layers in LEDs[6−14] and related devices.[15]

Unfortunately, when compared with electroluminescent materials such as PPVs, poly(*p*-phenylene)s (PPs), and polyfluorenes (PFs), the relatively low photoluminescence quantum yields (typically 1−3% in the solid state)[16] and poor electroluminescence performance of processable polythiophenes limit their applications in LEDs.[5,17] The low photoluminescence efficiency of polythiophenes is typically attributed to strong interactions between the polymer chains in the solid state,[6] as evidenced by the strong red-shifted absorbance of thin films in comparison to solution spectra.[4,5] Although such strong interchain interactions are an advantage for polythiophenes in some applications, they also enhance nonradiative decay via interchain processes and intersystem crossing caused by the heavy atom effect of sulfur, resulting in significantly reduced emission.[5,17f] Close-packed chains also improve the mobility of excitation, which increases the chance of finding quenching sites.[6]

Chart 1. Conjugated Homopolymers Used as LED Emissive Layers



Although other electroluminescent materials currently outperform polythiophenes in many ways, polythiophene-based materials allow good control of LED color[4] and can easily produce red colors, which are difficult to achieve with more common polymeric LED materials.[5] As a result, there is still considerable interest in the production of new processable polythiophene materials capable of high quantum efficiencies as well as efficient and balanced transport of both injected electrons and holes.[17f,18] One approach to enhancing the photoluminescence efficiency of polythiophenes has been the addition of aromatic arylene units to the polymer backbone, resulting in hybrid materials of polythiophene and polyaryl materials such as PP and PF.[17−22] Such materials have resulted in solid-state quantum efficiencies of ∼30% while also allowing tuning of the HOMO and LUMO energy levels of the resulting polymers.[17,20]

Another approach to the synthetic modification of polythiophenes is the introduction of fused aromatic units into the conjugated backbone, resulting in materials exhibiting enhanced carrier mobilities and lowered band gaps. One such fused-ring building block that has enjoyed recent popularity is the N-functionalized dithieno[3,2-*b*:2′,3′-*d*]pyrroles (DTPs).[23] Since their introduction, these building blocks have been incorporated into various

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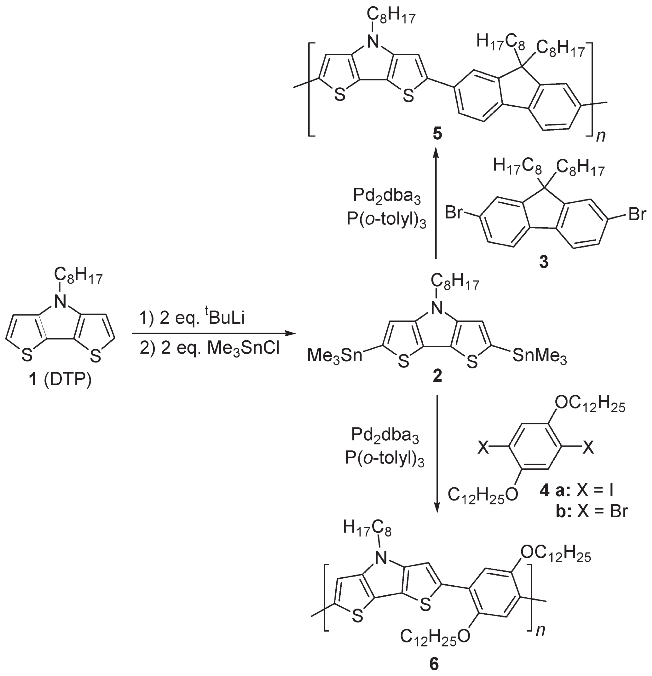
Scheme 1. Production of DTP Copolymers via Stille Coupling



polymeric,[24−34] oligomeric,[35−37] and molecular materials[38−40] to give high carrier mobilities, enhanced fluorescence, and materials with reduced and low band gaps. Because of the enhanced fluorescence properties exhibited by these materials, DTP-based materials could provide a potential new class of thiophene-based emissive layers for LEDs. To evaluate their potential for such applications, various DTP-arylene copolymers have been prepared and compared to the parent homopolymeric systems. The parent DTP homopolymer and the newly generated copolymers were then used as emissive layers to fabricate initial LEDs. The electronic and optical properties of the polymeric series are presented along with an initial evaluation of their device performance.

Results and Discussion

DTP copolymers **5** and **6** were prepared by Stille coupling as shown in Scheme 1. Previous attempts to form the dianion of DTP with mixtures of *n*-BuLi and TMEDA at cryogenic temperatures (i.e., −78 °C) were unsuccessful, thus requiring the use of *t*-BuLi.[35] However, more recent investigations have found that the application of BuLi/TMEDA mixtures at 0 °C can successfully produce the dianion, provided that an excess of the base mixture is used. In addition to the benefit of not requiring the more reactive alkyl lithium, the TMEDA seems to help solubilize the resulting salt, thus the dianion can be produced in more concentrated solutions than previously reported for the formation via *t*-BuLi.[35] Further treatment with Me$_3$SnCl then allows the efficient production of distannyl DTP **2**.

As previously reported, the distannyl intermediate is too unstable for extensive purification and undergoes decomposition on silica.[35] However, new methods have been developed in which the crude solution of **2** can be run through a plug of silica that has been partially deactivated with an Et$_3$N wash. Such treatment removes the inorganic byproducts generated during the formation of the distannyl intermediate, and rotary evaporation then removes the volatile organics. ^{1}H NMR of the resulting oil indicates the presence of trace amounts of residual tin species, which can be further removed by pumping down the sample overnight at 10−15 Torr. Such methods produce **2** as a pale-yellow oil (99%) with no detectable impurities by ^{1}H NMR that can be stored at low temperatures for several days before use.

Distannyl DTP **2** can then be cross-coupled via Stille coupling with dihaloaryls **3** and **4** to produce desired copolymers **5** and **6**, respectively. The polymerization reaction proceeds somewhat slowly, and optimum results were achieved for the production of **5** using a reaction time of 4 days. These conditions generated soluble material in yields of approximately 75%. An analysis of the resulting soluble material by GPC gives an M_n value of 10 500 with a PDI of 2.47. The use of shorter reaction times produced more soluble material but consisted of primarily oligomeric material. Extending the reaction time to 5 days increased the molecular weight of the soluble fraction (M_n = 16 900) but resulted in a greater amount of insoluble material and a decreased yield of usable material. An analogue of **5** has been previously reported by Qin and co-workers (**5**-Qin) and differs only in the DTP side chain (2-hexyldecyl rather than octyl).[28a] In contrast to that reported here, the production of this analogue, **5**-Qin, utilized Suzuki coupling and resulted in a significantly lower molecular weight species (M_n = 7500, PDI = 1.42). Although this may be a difference in the polymerization methods utilized, it has also been observed that the purity of the DTP precursors is critical for higher-molecular-weight materials. Potential differences in the resulting properties of **5** versus those of **5**-Qin will be further discussed below.

Similar to the production of copolymer **5**, the formation of phenylene analogue **6** was also slow and the optimum reaction time was again 4 days. In contrast, however, only 25% of quality soluble material could be obtained because of losses from both insoluble material and low-molecular-weight oligomeric products. Analysis by GPC after the removal of the low-molecular-weight products via Soxhlet washes gave a lower M_n value of 8200 with a PDI of 1.50. Attempts to increase both the yield and molecular weight by extending the reaction time to 5 days did reduce the oligomeric content but significantly increased the amount of insoluble material, resulting in no net increase in the yield of usable material and a slight decrease in M_n to 7600. As such, these M_n values of ~8000 may be the limit of solubility, and changes in the nature of the polymers' side chains may be required to achieve higher molecular weights. Attempts to modify the reaction conditions further by varying the halide on **4a** versus that on **4b** resulted in no significant changes.

The solution and thin film absorption spectra of DTP-based polymers **5**, **6**, and poly(*N*-decyldithieno[3,2-*b*:2′,3′-*d*]pyrrole) (PC$_{10}$DTP) are shown in Figure 1, and the combined optical and electronic properties are given in Table 1. Corresponding parent polymers regioregular poly(3-hexylthiophene)[2,41] (P3HT), poly(9,9-dihexylfluorene)[42] (PDHF), and poly(2-decyloxy-1,4-phenylene)[43] (PDP) as well as several related thiophene-arylene copolymers (Chart 2) are included for comparison. As previously reported, DTP homopolymers such as PC$_{10}$DTP exhibit much lower energy transitions than P3HT in solution, which could be attributed to a combination of the DTP's fused-ring nature and the electron-donating influence of the pyrrole nitrogen.[25] The fused-ring structure reduces rotational defects in solution, resulting in less coiling and a higher extent of conjugation. However, the lower-energy absorptions and reduced band gaps of DTP homopolymer thin films in comparison to those of P3HT suggest additional contributing factors. In addition to intrachain factors such as the electronic influence of the pyrrole nitrogen, DTP-based polymers exhibit enhanced interchain interactions as evidenced by their tendency to aggregate[27] and smaller π-stacking distances (3.6[27] vs 3.8 Å for P3ATs[44]).

For DTP copolymers **5** and **6**, the incorporation of arylene units into the backbone results in significant blue shifts in both the solution and solid-state absorption spectra. The same trends have been previously observed for various thiophene-arylene copolymers and have been explained to be due to changes in backbone planarity resulting from differences in energy barriers for thienyl−thienyl, thienyl−phenyl, and phenyl−phenyl rotations.[18a] However, it has also been proposed that the relative aromaticity of the units determines the strength of the confinement potential of the π electrons within the aromatic ring. Because the arylene species are more aromatic than thiophene, the electron confinement within the ring becomes stronger and the delocalization length along the polymer backbone decreases, thus resulting in larger band gaps.[3,45] Although blue-shifted in comparison to the parent DTP polymers, **5** and **6** exhibit solution absorption spectra that are red-shifted in comparison to analogous thiophene-arylene copolymers **7**−**9** as well as P3HT.

The solid-state spectra of **5** and **6** both exhibit a slight broadening of the absorption profile as well as the addition of a new low-energy peak resulting in a decrease in the energy of the onset of absorption. In comparison to related copolymers **7**−**9**, it can be seen that the addition of this low-energy peak occurs only in the DTP copolymers, most likely because of increased electron delocalization as a result of the stronger interchain coupling typical of DTP materials. However, unlike P3HT, the red shift of the energy onset upon film formation is rather small, thus the DTP copolymers exhibit larger band gaps than P3HT, with values of 2.2 and 2.0 for **5** and **6**, respectively. The lack of a large red shift from solution to the solid state is most likely due to the rodlike structure of the fused-ring materials in solution, resulting in little conformational change of the polymer backbone during film formation.[25]

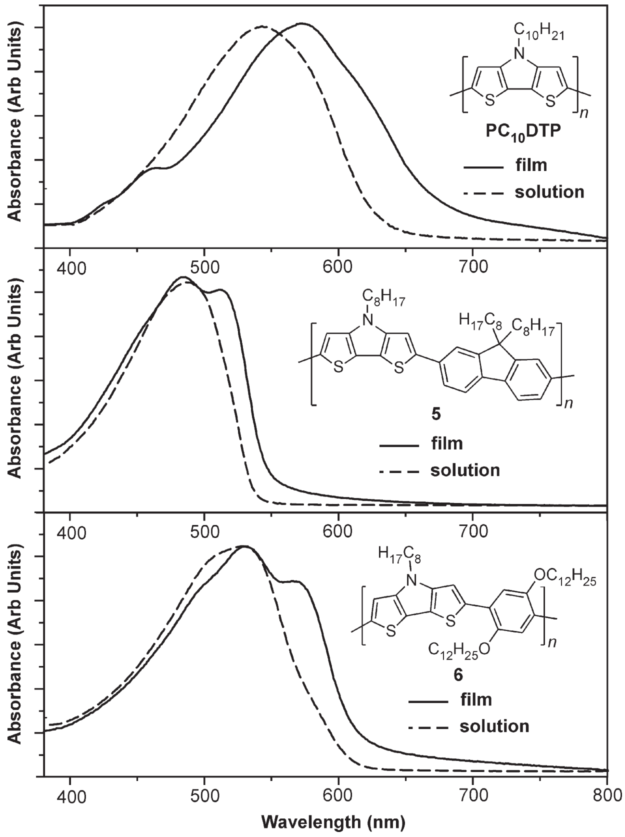


Figure 1. Solution and solid-state absorption spectra of DTP-based polymers.

As previously reported, DTP-based materials exhibit enhanced solution fluorescence in comparison to other functionalized thiophene materials.[25,35] However, the fluorescence quantum yields of the DTP-based polymers are still well below that of polyarylene systems such as PDHF (Table 1). As previously seen for other thiophene-based materials, the addition of arylene units results in further enhancements of the solution quantum yields as desired, with values of 0.50 and 0.37 for **5** and **6**, respectively. Of particular note, the comparison of **5** to the two thiophene-based analogues, **7** and **8**, shows that the application of DTP results in higher solution yields than previously possible with simple thiophenes. As can be seen in Figure 2, both DTP copolymers also retain the narrow emission bands previously observed for the DTP homopolymers.[25b] This narrowing of the transition is typical of the increased rigidity of the polymer backbone in solution,[46] which is also consistent with the relatively small red shifts exhibited in the solid-state spectra as discussed previously.

Although the application of DTP to conjugated materials effectively enhances the corresponding solution fluorescence, the increased planarity of the DTP-based species and the reported strong interchain interactions should favor close-packed structures[27] that would promote the additional quenching common in thin films. (Φ_F values of thin films are typically 10−10^3 times lower than for solution.[47]) In fact, this is exactly what is seen for the DTP homopolymers. In solution, these species exhibit strong fluorescence (Φ_F = 0.27−0.34),[25b] but this emission is strongly

Chart 2. Related Thiophene-Arylene Copolymers

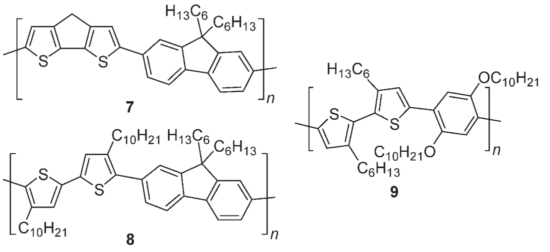


Table 1. Optical and Electronic Characteristics of Emissive Materials[a]

	solution			thin film					
polymer	$\lambda_{\max}^{\mathrm{abs}}$(nm)	$\lambda_{\max}^{\mathrm{em}}$(nm)	Φ_F	$\lambda_{\max}^{\mathrm{abs}}$(nm)	$\lambda_{\max}^{\mathrm{em}}$(nm)	Φ_F	E_g (eV)	E_{HOMO}	E_{LUMO}
P3HT[b]	456	570	0.26[c]	526, 556, 610	629[d]	0.02[e]	1.8	5.2	3.4
PC$_{10}$DTP[f]	552	614	0.31	572	[m]		1.7	4.6	2.9
PDHF[g]	384	417, 444	0.83	384	446, (483)	0.44	2.8		
5	487	531, (551)	0.50	484, 512	536, 567		2.2	5.3	3.1
5-Qin[h]	486	518, (549)	0.56	481, 510	536, 566	0.26	2.2	5.3	3.1
7[i]	443	516	0.40	438	523		2.5		
8[j]	401	482, (515)	0.31	403	490, (520)		2.5	6.1	3.6
PDP[k]				340	415	0.33	3.2	5.7	2.3
6	526	565	0.37	529, 566	601		2.0	5.1	3.1
9[l]				430	525	0.29	2.4	5.6	3.2

[a] P3HT = regioregular poly(3-hexylthiophene), PC$_{10}$DTP = poly(*N*-decyldecyldithieno[3,2-*b*:2',3'-*d*]-pyrrole, PDHF = poly(9,9-dihexylfluorene), and PDP = poly(2-decyloxy-1,4-phenylene). Solution data are given in CHCl$_3$, and values in parentheses are prominent shoulders. E_g = optical gap. E_{HOMO} was determined from the onset of oxidation vs ferrocene (5.1 eV vs vacuum). $E_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} - E_g$ [b] Reference 41b. [c] Boudouris, B. W.; Molins, F.; Blank, D. A.; Frisbie, C. D.; Hillmyer, M. A. *Macromolecules* **2009**, *42*, 4118. [d] Reference 9b. [e] Reference 16. [f] Reference 25b. [g] Reference 42. [h] Reference 28a. [i] Reference 21. [j] Reference 17e. [k] Reference 43. [l] Reference 17d. [m] Too weak to measure accurately.

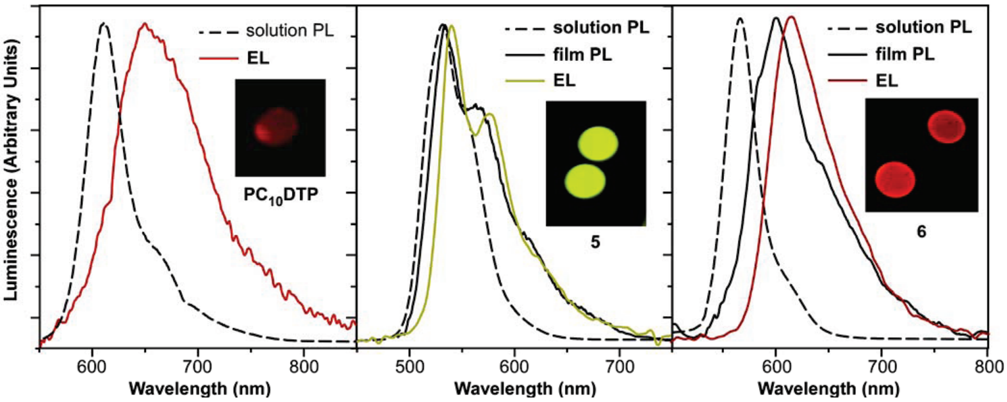


Figure 2. Solution and thin film photoluminescence (PL) and device electroluminescence (EL) of DTP-based polymers (emitting OLED devices shown in the inset).

Table 2. OLED Device Characteristics

polymer	film pl (nm)	device el (nm)	CIE chromaticity (*x*, *y*)	color emitted	$E_{\text{threshold}}$ (V)	max luminance (cd/m^2)
PC$_{10}$DTP	[a]	647	0.586, 0.336	red-purple	6.0	12
5	536, 567	541, 577	0.460, 0.528	yellow-green	5.2	197
6	601	647	0.626, 0.372	orange-red	5.9	30

[a] Too weak to measure accurately.

quenched in thin films. In fact, any potential solid-state emission for PC$_{10}$DTP is so weak that a thin film spectrum could not be accurately recorded with the facilities available. However, the thin film emission for the *N*-(2-hexyldecyl)DTP homopolymer has been recently reported to have its maximum at 655 nm and a corresponding solid-state Φ_F of 0.03.[28a] The use of the branched hexyldecyl side chain could perhaps hinder packing, thus resulting in higher solid-state emission, but comparative studies of side-chain branching effects on the solid-state emission of DTP oligomers have shown that singly branched side chains have little to no effect on enhancing solid-state emission.[35b] In addition, the reported quantum yield would make the DTP polymer a stronger solid-state emitter than P3HT ($\Phi_F = 0.02$),[16] which does not seem to be consistent with the known solid-state properties of the two polymer systems.[27] The fact that the same study reported a corresponding solution Φ_F value of 39%,[28a] ~10% higher than previously reported *N*-alkylDTP homopolymer quantum yields,[25b] may suggest a possible systematic error resulting in an overestimation of the measured quantum yields. Further evidence of the rigid DTP structure resulting in efficient solid-state quenching was reported by McCullough and co-workers in which seven DTP-thiophene copolymers were studied, with only one of which exhibiting any detectable solid-state emission ($\lambda_{\max} = 642$). In this study, it was proposed that the nonplanar head-to-head dialkylbithiophene unit in the one emitting species limited the extent of intermolecular interactions and thus reduced fluorescence quenching.[27]

In comparison to the DTP homopolymers and DTP-thiophene copolymers, DTP-arylene species **5** and **6** exhibit good thin film emission as shown in Figure 2. Here, the inclusion of the arylene unit should contribute weaker intermolecular interactions leading to a suppression of the strong interchain forces that lead to emission quenching. In the case of DTP-fluorene copolymer **5**, the highest intensity solid-state $\lambda_{\max}$ is only slightly red-shifted (5 nm) from solution, but the overall spectral profile has broadened, exhibiting good vibronic structure to give an additional peak at 567 nm and another shoulder further into the red. In contrast, DTP-phenylene copolymer **6** exhibits a larger red shift from solution (36 nm) and no significant vibronic structure, although broadening of the emission profile is also observed here.

As discussed above, Qin and co-workers previously reported closely related analogue **5**-Qin differing only in the nature of the DTP side chain.[28a] In comparison with **5**-Qin, the solution and solid-state absorption properties of **5** are very slightly red-shifted, consistent with the differences in molecular weight, but overall show good agreement. For the emission properties, however, greater differences are seen, and it is unclear whether this is just an effect of the differences in molecular weight or if there are other contributing factors. (See Supporting Information for spectral overlays of the two materials.) The reported quantum yield of **5**-Qin is also higher (by ~6%) than that of **5**, but this is consistent with the other high values reported in this study as discussed above.

To evaluate the potential of DTP-based materials as possible emissive layers for LEDs, initial devices with the configuration of ITO/PEDOT−PSS/emitting polymer/Alq$_3$/LiF/Al were fabricated using PC$_{10}$DTP and copolymers **5** and **6** as emitting layers. All three materials successfully resulted in working devices, although the emission from the PC$_{10}$DTP device was quite weak. The LED device characteristics are given in Table 2, and the resulting electroluminescence (EL) spectra and pictures of the emitting devices are shown in Figure 2.

The EL maximum for PC$_{10}$DTP is slightly blue-shifted in comparison to the thin film PL value of 655 nm reported by Qin,[28a] but the poor device performance is consistent with the efficient emission quenching in the thin films as discussed above. In comparison, the devices constructed from the copolymers give strong emission. For both **5** and **6**, the EL spectra are slightly red-shifted in relation to the corresponding thin film PL spectra, but with no significant changes in the emission profile. The emission energies of the three devices result in red-purple, yellow-green, and orange-red emission for the PC$_{10}$DTP, **5**, and **6** devices, respectively. Plots of current versus voltage for the three devices are shown in Figure 3A. In all cases, the threshold voltages are higher than the desired values of 5 V or below,[4] with the highest value observed at approximately 6 V for the PC$_{10}$DTP device. The threshold voltage for the **5** device, however, was more promising with a reduced value of 5.2 V. In addition, comparing the devices of both DTP copolymers (i.e., **5** and **6**) to devices of analogous bithienylarylene materials shows a significant reduction in the threshold voltages by utilizing DTP in place of bithiophene.[17f,18b]

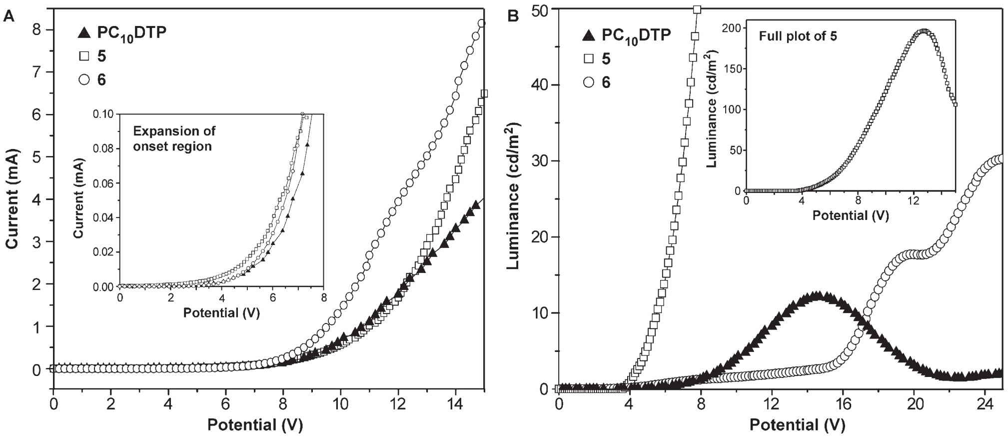


Figure 3. Current vs voltage (**A**) and luminance vs voltage (**B**) plots for the DTP-based LED devices.

The plots of the luminance versus voltage for the three devices are shown in Figure 3B. As can be seen, the homopolymer $PC_{10}DTP$ device demonstrates the lowest luminance, even when driven to quite high potentials. However, considering the significant quenching observed for the thin film photoluminescence, this is not unexpected and is in good agreement with the materials' photophysical properties. In comparison, the copolymer **5** device performed the best of the three systems studied and gave nearly 17 times the luminance at the same driving potential. In comparison to devices of analogous bithienylfluorene copolymers, the **5** device gave ~1.6 times the luminance (125 vs 197 cd/m^2),[18b] again showing the advantage of DTP over typical thiophene-based systems. The device constructed from **6** exhibited reasonable luminance, although it required quite high potentials to do so. Although the current initial devices are not optimized, they do illustrate the potential of the studied DTP-based materials, particularly that of **5** that exhibited a maximum efficiency of 0.8 Lm/W. Further tuning of the material properties (E_g, HOMO and LUMO levels, etc.) and modifications of the device structure could potentially improve these initial device characteristics.

In conclusion, DTP copolymers utilizing fluorene and phenylene units have been successfully synthesized via Stille coupling to give soluble, processable materials with good molecular weights. The resulting materials exhibit enhanced solution and thin film fluorescence in comparison to both the parent DTP polymers and P3HT. In comparison to previous analogous thiophene-arylene copolymers, the results presented here additionally illustrate that the application of DTP results in higher solution yields than previously possible with simple thiophenes. The processability and good solid-state emission properties of these copolymers make them promising emissive materials for LED applications, as demonstrated with the production of initial successful devices. Whereas initial color tuning has been demonstrated here through the relative arylene content of the material, future work will strive to extend the control of such tuning of the material properties. In addition to expanding the types of arylene units applied, tuning of materials through the application of the recently reported new class of *N*-acylDTP building blocks[23b] will also be explored. The application of such *N*-acylDTPs should allow materials with the benefits of the initial DTP-based materials reported here while also producing deeper HOMO levels and thus potentially better device performance.

Experimental Section

3,3′-Dibromo-2,2′-bithiophene[23b] and poly(*N*-decyldithieno-[3,2-*b*:2′,3′-*d*]pyrrole)[25b] were prepared as previously described. 2,7-Dibromo-9,9-dioctylfluorene (**3**) was prepared from 9,9-dioctylfluorene[48a] as previously described.[48b] Dry acetonitrile was distilled from CaH_2, and dry toluene was distilled from Na/benzophenone. All other materials were reagent grade and used without further purification. Chromatographic separations were performed using standard column methods with silica gel (230−400 mesh). All glassware was oven-dried, assembled hot, and cooled under dry N_2. All reactions were performed under dry N_2. ^1H NMR spectra were obtained in $CDCl_3$ on a 400 MHz spectrometer and referenced to the chloroform signal.

***N*-Octyldithieno[3,2-*b*:2′,3′-*d*]pyrrole (1).** DTP **1** was prepared from 3,3′-dibromo-2,2′-bithiophene using previously reported methods.[49] mp 34.6−35.2 °C. ^1H NMR: δ 7.138 (d, J = 5.4 Hz, 2H), 7.01 (d, J = 5.4 Hz, 2H), 4.19 (t, J = 7.2 Hz, 2H), 1.87 (m, 2H), 1.25 (m, 12H), 0.89 (t, J = 6.9 Hz, 3H). ^{13}C NMR: δ 145.2, 123.0, 114.9, 111.3, 47.7, 32.1, 30.7, 29.5, 29.4, 27.3, 22.9, 14.4. The NMR data agrees well with previously reported values.[23a]

***N*-Octyl-2,6-bis(trimethylstannyl)dithieno[3,2-*b*:2′,3′-*d*]pyrrole (2).** DTP **1** (0.302 g, 1.04 mmol) was added to a three-necked round-bottomed flask. Dry hexane (60 mL) was added, and the solution was cooled to 0 °C. TMEDA (0.45 mL, 3.0 mmol) was added, followed by *n*-BuLi (2.5 M in hexanes, 1.2 mL, 3.0 mmol), and the mixture was stirred for 2 h. Me_3SnCl (1.0 M in THF, 3.0 mL, 3.0 mmol) was then added, and the solution was stirred overnight. The mixture was then poured over Et_3N-treated silica gel, filtered, and rinsed with hexane. The filtrate was concentrated via rotary evaporation and pumped overnight to yield a pale-yellow oil (99% yield). The product was stored under N_2 in the freezer until further use. ^1H NMR: δ 7.00 (s, 2H), 4.18 (t, J = 7.2 Hz, 2H), 1.88 (p, J = 7.2 Hz, 2H), 1.35 (m, 2H), 1.27 (m, 8H), 0.87 (t, J = 7.2 Hz, 3H), 0.40 (s, 18H). ^{13}C NMR: δ 148.1, 131.4, 120.8, 118.2, 47.7, 32.1, 30.7, 29.4, 28.7, 27.3, 22.9, 14.3, −7.9.

1,4-Didodecyloxy-2,5-diiodobenzene (4a). Compound **4a** was prepared using methods previously reported for the preparation of 1,4-dihexadecyloxy-2,5-diiodobenzene, substituting dodecylbromide for hexadecylbromide.[50] Yield 84%. mp 66.3−67.2 °C. ^1H NMR: δ 7.17 (s, 2H), 3.92 (t, J = 7.2 Hz, 4H), 1.80 (p, J = 7.2 Hz, 4H), 1.49 (p, J = 7.2 Hz, 4H), 1.27 (m, 32H), 0.88 (t, J = 7.2 Hz, 6H). The ^1H NMR data agrees well with previously reported values.[51]

1,4-Dibromo-2,5-didodecyloxybenzene (4b). Compound **4b** was prepared using methods previously reported for the preparation of 1,4-dibromo-2,5-dioctyloxybenzene, substituting dodecylbromide for octylbromide.[52] Yield 52%. mp 73.0−74.6 °C (literature[53] 75−77 °C). ^1H NMR: δ 7.08 (s, 2H), 3.94 (t, J = 7.2 Hz, 4H), 1.80 (p, J = 7.2 Hz, 4H), 1.47 (p, J = 7.2 Hz, 4H), 1.26 (m, 32H), 0.88 (t, J = 7.2 Hz, 6H). The ^1H NMR data agrees well with previously reported values.[53]

Poly(*N*-octyldithieno[3,2-*b*:2′,3′-*d*]pyrrole-*alt*-9,9-dioctylfluorene) (5). To a 50 mL Schlenk tube was added **2** (0.578 g, 0.936 mmol), **3** (0.439 g, 0.800 mmol), Pd_2dba_3 (0.017 g, 0.019 mmol), and $P(o\text{-tolyl})_3$ (0.029 g, 0.075 mmol). Dry, N_2-purged toluene

(14 mL) was then added, and the reaction was placed in a 95 °C oil bath and allowed to react for 4 days. The resulting mixture was then precipitated into MeOH (300 mL), and the crude polymer was collected via vacuum filtration. The crude polymer was purified via Soxhlet extraction with MeOH, followed by acetone and then hexane. The soluble portion of the purified material was then isolated by washing with $CHCl_3$. Rotary evaporation of the $CHCl_3$-soluble fraction produced a deep-green solid (70−75%). ^1H NMR: δ 7.67, 7.61, 7.32, 4.28, 2.05, 1.50−0.80. GPC: $M_w = 34\,900$, $M_n = 13\,300$, and PDI = 2.62.

Poly(*N*-octyldithieno[3,2-*b*:2′,3′-*d*]pyrrole-*alt*-1,4-didodecyloxyphenylene) (6). Polymer **6** was prepared in the same manner as **5**, substituting **3** with either **4a** or **4b**. Rotary evaporation of the $CHCl_3$-soluble fraction produced a red-purple solid (20−25%). ^1H NMR: δ 7.67, 7.62, 7.30, 4.23, 1.97, 1.50−0.80. GPC: $M_w = 12\,400$, $M_n = 8200$, PDI = 1.50.

Gel Permeation Chromatography. All GPC experiments were performed on a 500 × 10 mm^2 Jordi Gel DVB 5 μm mixed-bed column with a Shimadzu SPD-M 10A VP UV absorbance PDA detector at 500 nm. Molecular weights were referenced to polystyrene standards. Polymer samples were prepared in THF (1 mg/mL) and passed through a 0.45 μm filter prior to injection. A constant flow rate of 1.5 mL/min was used.

Electrochemistry. All electrochemical methods were performed by using a three-electrode cell consisting of a platinum disk working electrode, a platinum wire auxiliary electrode, and a Ag/Ag^+ reference electrode (0.251 V vs SCE).[54] The supporting electrolyte consisted of 0.10 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dry CH_3CN. Solutions were deoxygenated by sparging with argon prior to each scan and blanketed with argon during the measurements. All measurements were collected at a scan rate of 100 mV/s. E_{HOMO} values were estimated from the onset of oxidation in relation to ferrocene (50 mV vs Ag/Ag^+) using the value of 5.1 eV versus vacuum for ferrocene.[55]

Preparation of Thin Films for Solid-State Spectroscopy. Polymer thin films were prepared by spin casting from saturated polymer solutions in THF or $CHCl_3$. The solutions were then loaded onto clean glass substrates (~1 × 2 cm^2) and spun at 1000 rpm for 120 s.

Absorption and Emission Spectroscopy. UV−vis spectroscopy was performed on a dual-beam scanning UV−vis−NIR spectrophotometer using samples prepared as dilute THF or CH_3Cl solutions in quartz cuvettes or as thin films on glass slides. Spectroscopy solvents were dried over molecular sieves prior to use. Solid-state absorption spectroscopy was conducted on thin films on glass substrates with reference to blank glass slides. Optical band gaps were defined by the onset of the lowest-energy transition, as determined by extrapolation of the steepest slope to the intersection with the spectral baseline.

Emission spectroscopy was performed using dilute, deoxygenated THF solutions at room temperature. Samples were excited at the absorption maximum, and all spectra were obtained by averaging five scans. Quantum yields were determined using secondary methods with 9,10-diphenylanthracene in deoxygenated cyclohexane as the reference.[56] Prior to each fluorescence measurement, the absorption spectrum was measured to ensure that the maximum absorption of the solution was less than 0.1. As the polymer data was collected in THF, corrections for the difference in the solvent refractive indices were applied using the following values: 1.426 for cyclohexane and 1.407 for THF. Solid-state spectra were obtained from thin films cast on glass substrates in which the emission was detected via a front face path rather than the standard right angle geometry and were not optimized for maximum measured intensities.

OLED Device Fabrication. Devices with the configuration of ITO/PEDOT−PSS/emitting polymer/Alq_3/LiF/Al were fabricated as follows. ITO coated 2 × 3 in.^{2} glass substrates were pretreated by ultrasonic rinsing sequentially in methanol, acetone, and IPA for 10 min each. The substrates were dried with a stream of dry air and then held at 150 °C for 2 h. Before deposition, the substrates were further cleaned under oxygen plasma for 7 min. The PEDOT−PSS (CLEVIOS P VP CH 8000; $R = (1-3) \times 10^5\ \Omega$ cm) layer was then deposited by spin casting at a speed of 2000 rpm for 1 min. The DTP-based polymer solution (5 mg/mL in anhydrous deoxygenated THF) was filtered through a 1.0 μm filter, deposited via spin casting (1000 rpm for 1 min) in a nitrogen glovebox ($O_2 < 1$ ppm) onto the PEDOT−PSS-coated ITO substrates, and annealed at 100 °C for 1 h. The electron-transport layer of Alq_3 (20 nm) was thermally evaporated under high vacuum with a base pressure of 6.4×10^{-6} Pa followed by a LiF (~1.5 nm) buffer layer. Because the thermal evaporation chamber was inside the same N_2 glovebox, the polymer layer was never exposed to air. After deposition, alumina crucibles containing Alq_3 and LiF were removed from the chamber and Al was deposited as the final layer with the LiF/Al bilayer acting as a cathode.

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Supporting Information Available: NMR spectra of **2**, full GPC data versus reaction time, absorption and emission spectral overlays of **5** versus **5**-Qin, and cyclic voltammograms of **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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