Macromolecules-

Fluorene–Dithienothiophene-S,S-dioxide Copolymers. Fine-Tuning for OLED Applications^{\perp}

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Supporting Information

ABSTRACT: Three groups of fluorene–dithieno[3,2-b;2',3'-d]thiophene-*S*,*S*-dioxides (DTT-*S*,*S*-dioxide) copolymers, each having four different ratios of DTT-*S*,*S*-dioxide (5, 15, 25, and 50%) were successfully synthesized through Suzuki coupling method. While the first group copolymers **P1** had direct connection of fluorene to the peripheral thiophenes of DTT-*S*,*S*-dioxide, second group copolymers **P2** had a thiophene extension between fluorene and DTT-*S*,*S*-dioxide, and in the third group, copolymers **P3**, fluorene had a connection with DTT-*S*,*S*-dioxide through the



phenyl moiety of DTT. Absorbance and emission measurements of first two groups P1 and P2 displayed a regular bathochromic shift with increasing content of DTT-*S*,*S*-dioxide, which was more clearly observed in their solid state fluorescence measurements. Introduction of thiophene to the peripherals of the DTT-*S*,*S*-dioxide in copolymers P2 caused even further bathochromic shift in absorbances and emissions. As the absorbance and emission of P1 went up to 447 and 558 nm in solution, respectively, P2 had them at 472 and 592 nm, respectively. In solid state, emissions of P1 and P2 even went further up to 585 and 646 nm, respectively. The bathochromic trend of P1 and P2 became opposite with absorbance and solid state emission of P3, which had a hypsochromic shift with increasing content of DTT-*S*,*S*-dioxide. Solid state emission of P3, particularly the copolymers having 5, 15 and 50% DTT-*S*,*S*-dioxide, covered a wide region between 400 and 675 nm. A spread of colors from light blue (border of white) to red through green and yellow was obtained with the OLED applications of the copolymers. Their optical and electronic band gaps varied between 2.17 and 2.99 eV and between 2.68 and 3.57 eV, respectively. While the highest quantum yield was obtained with P2 (5%) as 0.66, the lowest was observed with P2 (50%) as 0.03. Almost all of the polymers displayed good thermal stabilities. No weight loss was observed with the copolymers P2 (5–15%) and P3 up to 400 °C.

INTRODUCTION

Organic electronic materials, both small molecules and conjugated polymers, have been the focus of an increasing attention of academic and industrial research, particularly in chemistry and physics.¹ This is due to their possible applications in electronics and optoelectronics such as organic light-emitting diodes (OLED),² field-effect transistors (FET),³ lasers,⁴ photodiodes,⁵ and solar cells.⁶ The main attraction of this field comes from the ability to modify the chemical structure of organic compounds in a way that the properties of the materials could directly be affected. Moreover, some important tunings in structure or composition of an organic material can markedly alter its bulk properties. Understanding of their electronic structure is the key to the design of high performance optical and electronic organic devices. Currently, modification of the molecular structure of the conjugated materials to tune their optoelectronic properties is a challenging topic,^{1a} among which, thiophene based organic materials are the most promising compounds to be modified by proper molecular engineering as they have tunable functional properties.⁷ For example, thiophenes and their oligomers and polymers are not proper materials for applications in light

emitting devices as they have low electron affinities and low solid-state photoluminescence efficiencies.^{8–14} On the other hand, converting oligothiophenes into the corresponding oligothiophene-*S*,*S*-dioxides has been shown to be useful for increasing both thin film photoluminescence efficiencies and molecular energy levels.^{7c,14–16}

In recent years, syntheses and investigations of the properties of dithieno[3,2-b;2',3'-d]thiophenes (DTT) (1), DTT-*S*,*S*dioxides (2), and their polymers have been the emerging area as they show interesting electronics and optoelectronics properties.¹⁷ DTTs comprise three fused thiophene rings which create an electron rich rigid core. Oxidation of the sulfur atom of the central thiophene to the *S*,*S*-dioxide introduces the molecule a fluorescent property with, in general, an emission in the blue region. Our continuing research on the synthesis of analogues of DTT, applying the method developed by our group, let us to the syntheses of functionalized DTT analogues, such as 3,5-diphenylDTT (3), 3,5-di(4-bromophenyl)DTT (4),

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3,5-di(4-methoxyphenyl)DTT (5), and 3,5-di(4-nitrophenyl)-DTT (6),¹⁸ oxidation of which yield their fluorescent derivatives. As copolymerization of thiophenes with various monomers is an important strategy for fine-tuning the resultant material,⁷ in this study, Ph₂DTT-*S*,*S*-O₂ (7), (BrPh)₂DTT-*S*,*S*-O₂ (8), and Br₂Ph₂Th₂DTT-*S*,*S*-O₂ (14) were copolymerized with a commonly used monomer, fluorene, in different ratios of DTTs, i.e., 5%, 15%, 25%, and 50%, considering that such ratios could be a good tuning for the synthesized materials for OLED applications. Their devices were fabricated and the properties of the polymers in solution, in solid state and the properties of their devices were investigated.

EXPERIMENTAL SECTION

2-Bromo-9,9-dioctyl-9H-fluorene (F1), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (15), 2,7-dibromo-9,9-dioctyl-9H-fluorene (16), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-9,9-dioctylfluorene (17), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-[1,3,2]dioxaborolane (13),¹⁹ and poly[2,7-(9,9-dioctylfluorene)] (F)²⁰ were synthesized according to the literature procedures.

Materials. *N*-Bromosuccinimde (NBS), thiophene, dichloromethane (DCM), and *N*,*N*-dimethylformamide (DMF) were purchased from Merck. *m*-Chloroperbenzoic acid (mCPBA) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were obtained from Sigma-Aldrich. All chemicals were used as received unless it is stated. Quantum yield measurements of the polymers, dissolved in THF, were performed using coumarin1 (quantum yield = 0.73, excited at 360 nm, in ethanol), coumarin6 (quantum yield = 0.78, excited at 420 nm, in ethanol), and quinine sulfate (quantum yield = 0.546, excited at 310 nm, in 0.5 M H₂SO₄) as standards

Instrumentation. Cyclic voltammetry (CV) studies were performed using CH-Instruments Model 400A as a potentiostat. UV-vis measurements were studied on HITACHI U-0080D. ¹H and ¹³C NMR spectra were recorded on Varian model NMR (600 MHz). Proton and carbon chemical shifts were reported in ppm downfield from tetramethylsilane (TMS). Mass spectra were recorded on Bruker MICROTOFQ and Thermo LCQ-Deca ion trap mass instruments. The molar mass and molar mass distribution of the polymers were determined by gel permeation chromatography (GPC), equipped with Perkin-Elmer 200 GPC high pressure pump, injector, THF columns connected in series (guard column + Styragel HR2 + Styragel HR3 + Styragel HR 4E + Styragel HR 5E), Wyatt Optilab differential refractive index detector (RI) at 654 nm, and Dawn Heleos multi angle light-scattering (LS) detector. The mobile phase was THF with a flow rate of 0.7 mL/min. Measurements were conducted at 25 °C. Polymer concentrations were in the range of 0.5-2.0 mg/mL and all the samples were filtered through 0.2 μ m filter prior to use. Thermal analyses (TA) of the polymers were performed by a Perkin-Elmer thermal analyzer system equipped with Pyris 6 model thermogravimetry and Jude differential scanning calorimetry (DSC) systems.

Device Fabrication and Characterization. ITO-coated glass substrates (ITO, thickness 120 nm, 15 ohms/sq) were purchased from Visiontek Systems. Poly(3,4-ethylenedioxythiophene) poly-(styrenesulfonate) (PEDOT:PSS) was obtained from Heraeus Clevios GmbH. All the copolymers were prepared by dissolving them in a mixture of toluene/dichlorobenzene, having a concentration of 8 mg/mL, and filtered through a 0.45 μ m membrane filter (Millipore, PTFE). The substrates were etched in aqua regia solution (3:1:3/HCl:HNO₃:H₂O) for 2 min, and then cleaned consecutively in ultrasonic baths containing deionized water, acetone, and isopropyl

alcohol. Lastly, the substrates were dried under N₂ flow. PEDOT:PSS, as a hole injection layer, was spin-coated at 3000 rpm for 30 s, which was then dried at 110 °C for 10 min. Subsequently, the polymer films, as active layers, were produced by spin coating at 1200 rpm and cured at 120 °C for 5 min. Finally, calcium (Ca, 6 nm) and aluminum (Al, 100 nm) were deposited under vacuum (~5 × 10⁻⁶ bar) by thermal evaporation technique, as a cathode layer. The active emission area was 9 mm². Electroluminescence, brightness–voltage, luminous efficiency and EQE–current density curves of the fabricated OLEDs were obtained by a Hamamatsu PMA-12 C10027 photonic multichannel analyzer and a digital multimeter (2427-C 3A Keithley). All the devices were measured in a dark sample chamber to remove any influence of ambient light. A stylus profiler (KLA Tencor $P\overline{6}$) was used to determine the thickness of the organic layers.

3,5-Diphenyldithieno[3,2-b;2',3'-d]thiophene-5,5-dioxide (7). To a solution of 3 (0.2 g, 0.57 mmol), dissolved in DCM (30 mL), was added dropwise mCPBA (0.51 g, 2.3 mmol) dissolved in DCM (15 mL) at 0 °C. The reaction was then left stirring overnight at room temperature for 2 days. The solution was extracted with 10% KOH, 10% NaHCO₃ and brine. Organic layer was dried over Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography, eluting with a mixture of hexane/DCM (3:1) to give the title compound (7) (0.16 g, 72%) as a yellow powder, mp 187–190 °C. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.83 (dd, J = 7.6 Hz, 1.2 Hz, 4H), 7.47 (t, J = 7.6Hz, 4H), 7.40 (t, J = 7.6 Hz, 2H), 7.36 (s, 2H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 141.1, 139.2, 137.0, 131.9, 129.2, 128.9, 127.8, 124.2. m/z = 381.00 (M⁺ + 1).

3,5-Bis(4-bromophenyl)dithieno[3,2-b;2',3'-d]thiophene-S,S-dioxide (8). It was synthesized similar to 7, starting from 4. The crude product was purified by column chromatography, eluting with a mixture of hexane/DCM (1:1) to give the title compound (8) (0.07 g, 34%) as a yellow powder, mp 273–275 °C. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.68 (d, J = 8.2 Hz, 4H), 7.60 (d, J = 8.2 Hz, 4H), 7.35 (s, 2H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 140.0, 137.9, 137.1,132.4, 130.1, 129.3, 124.7, 123.4. m/z = 539 (M⁺ + 1).

2,6-Dibromo-3,5-diphenyldithieno[3,2-b;2',3'-d]thiophene (9). To a solution of 3 (0.2 g, 0.57 mmol) dissolved in DMF (20 mL) and protected from light was added 0.22 g NBS (0.22 g, 1.26 mmol) portionwise at 0 °C. After 7 h, the reaction mixture was poured into cold water to precipitate the crude product, which was recrystallized from toluene to give the title compound (9) (0.24 g, 83%) as a white powder, mp 241–242 °C. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.67 (d, *J* = 7.5 Hz, 4H), 7.50 (t, *J* = 7.5 Hz, 4H), 7.43 (t, *J* = 7.5 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 139.8, 134.9, 133.2, 129.3, 128.9, 128.7, 128.6, 108.8. *m*/*z* = 506 (M⁺).

2,6-Dibromo-3,5-bis(4-bromophenyl)dithieno[3,2-b;2',3'-d]thiophene (10). It was synthesized similar to 9, starting from 4. The crude product was recrystallized from toluene to give the title compound (10) (0.23 g, 87%) as a white powder, mp 309–312 °C. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.62 (d, J = 8.4 Hz, 4H), 7.53 (d, J = 8.4 Hz, 4H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 139.7, 136.1, 132.5, 132.1, 131.0, 128.7, 124.0, 113.6. m/z = 667 (M⁺ + 1).

2,6-Dibromo-3,5-diphenyldithieno[3,2-b;2',3'-d]thiophene-5,5dioxide (11). It was synthesized similar to 7, starting from 9. The crude product was purified by column chromatography, eluting with a mixture of hexane/DCM (1:1) to give the title compound (11) (0.19 g, 90%) as a yellow powder, mp 220–222 °C. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.68 (dd, J = 7.8 Hz, 1.2 Hz, 4H), 7.47 (t, J = 7.8Hz, 4H), 7.44 (t, J = 7.8 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 140.3, 137.3, 134.1, 129.9, 129.4, 129.3, 128.8, 113.1. m/z =539 (M⁺ + 1). 2,6-Dibromo-3,5-bis(4-bromophenyl)dithieno[3,2-b;2',3'-d]thiophene-S,S-dioxide (12). It was synthesized similar to 8, starting from 10. The crude product was purified by column chromatography, eluting with a mixture of hexane/DCM (2:1) to give the title compound (12) (0.17 g, 83%) as a yellow-orange powder, mp 284– 287 °C. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.53 (d, J = 9 Hz, 4H), 7.48 (d, J = 9 Hz, 4H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 140.0, 136.1, 134.2, 132.1, 131.0, 128.7, 124.0, 113.6. m/z = 697 (M⁺ + 1).

2,6-Bis(5-bromothiophen-2-yl)-3,5-diphenyldithieno[3,2-b;2',3'd]thiophene-S,S-dioxide (14). In a Schlenk tube, a mixture of 11 (0.2 g, 0.37 mmol), 13 (0.2 g, 0.93 mmol), Pd(PPh₃)₄ (0) (0.02 g, 0.02 mmol), and K₂CO₃ (1 mL, 2 M) in THF (50 mL) was degassed with N2 for half an hour. Then, the mixture was sealed and stirred at 68 °C for 2 days. It was filtered through Celite and the crude product was purified by column chromatography, eluting with a mixture of hexane:DCM (2:1). The product was subsequently dissolved in DMF and reacted with NBS. The mixture was poured into cold water and the precipitate was filtered. It was dissolved with a minimum amount of DCM, precipitated in diethyl ether and filtered to obtain the title compound 14 (0.20 g, 76%) as an orange powder, mp 300-303 °C. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.52 (d, J = 4 Hz, 4H), 7.40 (t, J = 4 Hz, 6H), 6.92 (d, J = 3.6 Hz, 2H), 6.81 (d, J = 3.6 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 143.0, 135.5, 135.4, 134.2, 132.6, 130.3, 130.2, 129.7, 129.3, 129.0, 127.8, 114.6. *m*/*z* = 703 $(M^+ + 1).$

General Method for the Syntheses of the Polymers P1-5. A mixture of 11 (0.023 mmol, 12.4 mg), 15 (0.232 mmol, 150 mg), 16 (0.209 mmol, 114.4 mg), K_2CO_3 (1 mL, 2 M) and $Pd(PPh_3)_4$ (0.001 mmol, 12 mg) (Table 1) in a solvent mixture of toluene:dioxane (9:1,

 Table 1. Ratios of the Contents for the Syntheses of the
 Polymers P1

entry	P1-5	P1-15	P1-25	P1-50
11	0.023 mmol	0.063 mmol	0.116 mmol	0.232 mmol
	(12.4 mg)	(34 mg)	(62.4 mg)	(124.9 mg)
15	0.232 mmol	0.232 mmol	0.232 mmol	0.232 mmol
	(150 mg)	(150 mg)	(150 mg)	(150 mg)
16	0.209 mmol (114.4 mg)	0.169 mmol (92.7 mg)	0.116 mmol (63.6 mg)	-
K ₂ CO ₃ (2 M)	1 mL	1 mL	1 mL	1 mL
$Pd(PPh_3)_4$	0.001 mmol	0.001 mmol	0.001 mmol	0.001 mmol
	(12 mg)	(12 mg)	(12 mg)	(12 mg)
17	0.068 mmol	0.068 mmol	0.068 mmol	0.068 mmol
	(35 mg)	(35 mg)	(35 mg)	(35 mg)
F1	0.074 mmol	0.074 mmol	0.074 mmol	0.074 mmol
	(35 mg)	(35 mg)	(35 mg)	(35 mg)

5 mL) in a Schlenk tube was degassed with N₂ and sealed. The mixture was stirred for 2 days, and 17 (0.068 mmol, 35 mg) was then added. Stirring was continued for 1 day. Lastly, F1 (0.074 mmol, 35 mg) was added and the mixture was stirred one more day. The reaction mixture was filtered through Celite and the solvent was evaporated under reduced pressure. The crude product was dissolved in a minimum amount of THF and precipitated in methanol. P1-5: 81% yield; M_{wr} , 313 900; M_n , 83 640; M_w/M_n , 3.75; dn/dc, 0.13 mL/g. P1-15: 76% yield; M_{wr} , 69 840; M_n , 27 330; M_w/M_n , 2.55; dn/dc, 0.17 mL/g. P1-25: 73% yield; M_{wr} , 40 110; M_n , 23 620; M_w/M_n , 1.70; dn/dc, 0.20 mL/g. P1-50: 83% yield; M_{wr} , 859 100; M_n , 699 600; M_w/M_n , 1.23; dn/dc, 0.14 mL/g.

The following were prepared similarly.

Synthesis of P2 (Table 2). P2-5: 83% yield; M_{w^2} 37 060; M_n , 27 760; M_w/M_n , 1.33; dn/dc, 0.11 mL/g. **P2-15**: 87% yield; M_w , 501 200; M_n , 219 200; M_w/M_n , 2.29; dn/dc, 0.16 mL/g. **P2-25**: 78% yield; M_{w^2} 102 200; M_n , 76 210; M_w/M_n , 1.34; dn/dc, 0.19 mL/g. **P2-50**: 81% yield; M_{w^2} 60 630; M_n , 43 680; M_w/M_n , 1.39; dn/dc, 0.21 mL/g.

Synthesis of P3 (Table 3). P3-5: 48% yield; M_w , 9567; M_n , 8261; M_w/M_n , 1.16; dn/dc, 0.149 mL/g. P3-15: 44% yield; M_w , 71 200; M_n ,

 Table 2. Ratios of the Contents for the Syntheses of the

 Polymers P2

entry	P2-5	P2-15	P2-25	P2-50
14	0.023 mmol	0.063 mmol	0.116 mmol	0.232 mmol
	(16.1 mg)	(44.3 mg)	(81.5 mg)	(163 mg)
15	0.232 mmol	0.232 mmol	0.232 mmol	0.232 mmol
	(150 mg)	(150 mg)	(150 mg)	(150 mg)
16	0.209 mmol (114.4 mg)	0.169 mmol (92.7 mg)	0.116 mmol (63.6 mg)	_
$\begin{array}{c} K_2CO_3 \ (2\ M) \end{array}$	1 mL	1 mL	1 mL	1 mL
$Pd(PPh_3)_4$	0.001 mmol	0.001 mmol	0.001 mmol	0.001 mmol
	(12 mg)	(12 mg)	(12 mg)	(12 mg)
17	0.068 mmol	0.068 mmol	0.068 mmol	0.068 mmol
	(35 mg)	(35 mg)	(35 mg)	(35 mg)
F1	0.074 mmol	0.074 mmol	0.074 mmol	0.074 mmol
	(35 mg)	(35 mg)	(35 mg)	(35 mg)

Table 3. Ratios of the Contents for the Syntheses of the Polymers P3

entry	P3-5	P3-15	P3-25	P3-50
8	0.023 mmol	0.063 mmol	0.116 mmol	0.232 mmol
	(12.4 mg)	(34 mg)	(62.4 mg)	(124.9 mg)
15	0.232 mmol	0.232 mmol	0.232 mmol	0.232 mmol
	(150 mg)	(150 mg)	(150 mg)	(150 mg)
16	0.209 mmol (114.4 mg)	0.169 mmol (92.7 mg)	0.116 mmol (63.6 mg)	-
K ₂ CO ₃ (2 M)	1 mL	1 mL	1 mL	1 mL
$Pd(PPh_3)_4$	0.001 mmol	0.001 mmol	0.001 mmol	0.001 mmol
	(12 mg)	(12 mg)	(12 mg)	(12 mg)
17	0.068 mmol	0.068 mmol	0.068 mmol	0.068 mmol
	(35 mg)	(35 mg)	(35 mg)	(35 mg)
F1	0.074 mmol	0.074 mmol	0.074 mmol	0.074 mmol
	(35 mg)	(35 mg)	(35 mg)	(35 mg)

47 180; M_w/M_n , 1.51; dn/dc, 0.1691 mL/g. **P3-25**: 53% yield; M_w , 24 710; M_n , 6863; M_w/M_n , 3.60; dn/dc, 0.80 mL/g. **P3-50**: 36% yield; M_w , 16 310; M_n , 7694; M_w/M_n , 2.12; dn/dc, 0.26 mL/g.

RESULTS AND DISCUSSION

Syntheses. DTTs **3** and **4** were prepared following the literature procedures.^{18,21,22} While oxidation of the DTTs with mCPBA produced dithienothiophene-*S*,*S*-dioxides (DTT-*S*,*S*- O_2) **7** and **8**, which were dibrominated with NBS to yield the dibromodithienothiophene-*S*,*S*-dioxides (Br₂DTT-*S*,*S*- O_2) **11** and **12**, respectively, bromination of the DTTs with NBS gave dibromo-DTTs (Br₂DTT) **9** and **10**, which were also oxidized to obtain **11** and **12**, respectively (Scheme 1). Suzuki coupling of Br₂DTT-*S*,*S*- O_2 (**11**) with 4,4,5,5-tetramethyl-2-thiophen-2-yl-[1,3,2]dioxaborolane (**13**)¹⁹ was followed by bromination with NBS to yield the monomer **14**.

The monomers **11**, **14**, and **8** were subjected to polymerization with flouorenes **15** and **16** in four ratios of 5, 15, 25, and 50% to obtain three series of DTT-*S*,*S*-dioxide-fluorene random copolymers **P1**, **P2**, and **P3**, respectively. All the polymerization reactions were performed applying Suzuki coupling technique, which yielded three groups, each having four polymers and totaling to 12 polymers (**P1-5**, **P1-15**, **P1-25**, **P1-50**; **P2-5**, **P2-15**, **P2-25**, **P2-50** and **P3-5**, **P3-15**, **P3-25**, **P3-50**) (Scheme 2). The ratios of DTT-*S*,*S*-dioxides in the fluorene polymers were described with the integration ratios of the aromatic peaks to the alphatic peaks of the carbon chains on the flurenes (see Supporting Information). Moreover, particularly the solid state

Scheme 1. Syntheses of the DTTs



Scheme 2. Syntheses of DTT-Fluorene Copolymers (P1, P2, and P3)



fluorescence measurements displayed distinct peaks for each polymer.

Optical and Electrochemical Properties of the Polymers. Optical properties of the polymers were investigated in solution (THF) and solid state, spin coated on glasses. Absorbance spectra of the polymers **P1** displayed that the polymer having 5% of DTT-*S*,*S*-dioxide **P1-5** (382 nm) had almost the same absorbance with polyfluorene **F** (383 nm) (Figure 1a, Table 4). Upon increasing the content of DTT-*S*,*S*dioxide in the polymer, appearance of a peak around 430 nm took place, which became gradually stronger at higher contents of DTT-*S*,*S*-dioxide and reached maximum with **P1-50**, containing 50% of DTT-*S*,*S*-dioxide, as the absorbance of fluorene reached minimum. These results demonstrated that two absorbencies varying with the contents of fluorene and DTT-*S*,*S*-dioxide, were obtained at around 380 and 430 nm, respectively. Fluorescence measurements followed the same trend. Two emission bands around 420 nm due to fluorene and between 443 and 558 nm due to DTT-*S*,*S*-dioxide were observed (Figure 1b, Table 4). As the content of DTT-*S*,*S*-



Figure 1. UV-vis (a) and fluorescence (b) measurements of P1 in THF and emission in films from THF (c).

Table 4. Electrochemical, Optical, and Electronic Properties of the Po
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sample	abs. λ_{\max}^{a}	emission $\lambda_{\max}^{\ \ b}$	QY	abs. λ_{\max}^{c}	emission λ_{\max}^{d}	$E_{\rm g}^{\rm opt}$	HOMO ^h	LUMO ⁱ	E_{g}^{cv}
F	383	420, 443 ^{sh}	0.78 ^e	360	422 ^{sh} , 436, 463 ^{sh} , 528	2.98	-5.74	-2.26	3.48
P1-5	382	421, 444 ^{sh}	0.38 ^e	387	545	2.95	-5.81	-2.49	3.32
P1-15	380	421, 445	0.15 ^e	399	561	2.48	-5.81	-2.27	3.54
P1-25	374, 430 ^{sh}	419, 436 ^{sh} , 535	0.12^{e}	412	575	2.47	-5.74	-2.30	3.44
P1-50	343, 447	420, 448 ^{sh} , 558	0.08^{f}	426	585	2.47	-5.78	-3.10	2.68
P2-5	375	419, 442 ^{sh}	0.66 ^e	372, 485	620	2.95	-5.81	-2.24	3.57
P2-15	369, 445	418, 440 ^{sh} , 589	0.30 ^e	379, 489	631	2.26	-5.65	-2.57	3.08
P2-25	307, 360, 449	418, 440 ^{sh} , 589	0.12^{e}	380, 494	636	2.26	-5.66	-2.61	3.05
P2-50	318, 342 ^{sh} , 472	400, 592, 725 ^{sh}	0.03 ^e	364, 475	646	2.17	-5.60	-3.22	2.38
P3-5	377	418, 442 ^{sh}	0.56 ^e	410	439, 465, 500	2.99	-5.72	-2.44	3.28
P3-15	376	423, 446	0.17^{e}	397	420, 440, 465, 498	2.97	-5.73	-2.36	3.37
P3-25	368	420, 447	0.12^{g}	383	413, 438, 518	2.97	-5.82	-2.34	3.48
P3-50	340	461	0.09 ^g	364	470, 496	2.97	-5.89	-2.83	3.06

^{*a*}Absorbtion in THF. ^{*b*}Emission in THF. ^{*c*}Absorption maxima of the polymer films coated on ITO ^{*d*}Emission maxima of the polymer films coated on ITO. ^{*e*}Quantum yield calculated using Coumarin1 as a standard in ethanol. ^{*f*}Quantum yield calculated using Coumarin6 as a standard in ethanol. ^{*g*}Quantum yield calculated using quinine sulfate as a standard in 0.5 M H₂SO₄. ^{*h*}HOMO = $-E_{onset}$ (ox) + (4.4) (eV). ^{*i*}LUMO = $-E_{onset}$ (red) + 4.4 (eV).



Figure 2. UV-vis (a) and fluorescence (b) measurements of P2 in THF and emission in films from THF (c).

dioxide was increased, the second peak became stronger. On the other hand, in solid state, a different trend was displayed (Figure 1c). While polyfluorene F gave two emission bands at 436 and 528 nm, the rest of the polymers had one emission band. Effect of the increasing content of DTT-*S*,*S*-dioxide on a regular red shift emission was clearly observed in solid state fluorescent measurements. Although absorbance and emission bands of polyfluorene and the polymer having 5% of DTT-*S*,*S*dioxide **P1-5** in THF were nearly the same, a clear difference was displayed with a 17 nm red shift of **P1-5** in solid state.

As the phenyl groups at C-3 and C-5 of DTT could restrict conjugation through the polymer chain by blocking free rotations between two DTT or DTT-florene moieties, thiophenes were introduced to the peripherals of DTT to obtain the polymers **P2**. A substantial red sift and a wide range of absorbance between 300–600 nm of the polymers **P2-15**, **25**, and **50** were observed, which implied that a better rotation and a good conjugation have been provided (Figure 2a, Table 4). Fluorescence measurements in THF displayed that as the polymer **P2-5** gave a similar emission with polyfluorene **F**, the rest had emission maxima around 600 nm, ranging from 500 to 750 nm (Figure 2b). The polymers **P2**, like the polymers **P1**, displayed quite different behaviors in solid state emissions (Figure 2c). A similar emission of **P2-5** with **F** in THF did not take place in solid state, rather a similar emission trend of **P1** was observed. This time an emission difference of 92 nm took place between **F** and **P2-5**. While **F** displayed an emission maxima at 528 nm, the polymers **P2-5**, **P2-15**, **P2-25**, and **P2-50** had a regular emission maxima of 620, 631, 636, and 646 nm, respectively, in line of increasing DTT-S,S-dioxide contents.

Lastly, optical properties of the polymers P3, obtained through the polymerization of DTT-S,S-dioxide from its phenyl groups with fluorene in 5, 15, 25 and 50% ratios, were

1.0

0.5

0.0

300

Normalized Absorbance

Wavelength (nm)

Figure 3. UV-vis (a) and fluorescence (b) measurements of P3 in THF and emission in films from THF (c).

investigated (Figure 3, Table 4). As the conjugation through phenyl group is not as effective as through the thiophenes, absorbances of P3 had a similar behaviors with polyfluorene F (Figure 3a), and as the content of DTT-S,S-dioxide was increased, a hypsochromic shift at the absorbances was observed, which was more distinct with the polymers P3-25 and P3-50, having 25 and 50% of DTT-S,S-dioxide with absorbance maxima of 368 and 340 nm, respectively. This proves that increasing content of DTT-S,S-dioxide provides less conjugation. Investigation of emission behaviors of the polymers P3 indicated that while the polymers had red shift (bathochromic) emission in THF with the increasing content of DTT-S,S-dioxide, a reverse situation, a blue shift (hypsochromic) from fluorene, generally with decreasing content of DTT-S,S-dioxide was observed. This could be the result of polyfluorene tending to emit light around 550 nm and DTT-S,S-dioxide polymerized through its phenyl groups having emission behavior around 440 nm in solid state (Figure 3c, Table 4). The emission of P3-50 almost covered whole region from 400 extending to 700 nm, which indicates that emission properties of both fluorene and DTT-S,S-dioxide were combined under a wide curve.

Wavelength (nm)

Cyclic voltammetry (CV) behaviors of the polymers P1-P3 were investigated in dry and degassed acetonitrile, using Bu₄NPF₆ as an electrolyte, under nitrogen atmosphere, by drop-casting onto glassy carbon disc electrode from their THF solutions (Figure 4, Table 4 and see Supporting Information). Pt wire and Ag/AgCl were counter and reference electrodes, respectively. Bandgaps of the polymers were calculated to be between 2.38 and 3.57 eV from the differences between the onsets of oxidation and reduction peaks, scanning between (-2.5) and (+2) V. Their optical bandgaps varied between 2.17 and 2.99 eV (Table 4).



Figure 4. Cyclic voltammograms of the polymers P1 on glassy carbon disk electrode in acetonitrile, 0.1 M Bu₄NPF₆, 500 mV/s scan rate.

Thermal Gravity Analyses of the Polymers. Thermal analyses of the polymers indicated that although all the polymers had good thermal stability, the best stabilities, i.e. up to 400 °C, were obtained with the polymers P2-5, 15, 25, and P3 (Figure 5). While increasing content of DTT-S,S-dioxide

Wavelength (nm)

400



Figure 5. Thermal gravity analyses of the polymers P1-P3.

effected thermal stability of the polymers P1 and P2-50, bringing start of their weight loss to 170 and 280 °C, respectively, such a loss was not observed with P2-5, 15, 25, and P3 up to around 400 °C. When the thermal behaviors of the polymers P1 and P2 were investigated more closely, initial degradation temperatures of the polymers P1-50 and P2-50, having fluorene/DTT-S,S-dioxide ratio of 1:1, were observed to be at lower temperatures. On the other hand, such a weight loss was not observed with P3-50, which had the same ratio of fluorene/DTT-S,S-dioxide (1:1). This result could be due to the polymerization through the phenyl-phenyl linkage in polymer P3-50.

Device Characterization. OLED devices based on the device architecture of ITO/PEDOT:PSS (50 nm)/copolymer (60 nm) (P1, P2, or P3)/Ca (6 nm)/Al (100 nm) structure were fabricated and their properties-luminance (brightness), luminous efficiency, and external quantum efficiency-were investigated.

Luminance and both luminous and quantum efficiencies of the polymers P1 were significantly changed with varying content of DTT-S,S-dioxides, which were improved with increasing DTT-S,S-dioxides up to 25% (Figure 6, Table 5). Although the maximum efficiency values of devices P1-5 and P1-15 were found to be similar (0.100 and 0.104 cd/A), P1-15 reached its maximum at a relatively low current density.

700



Figure 6. (a) Luminance-voltage, (b) luminous efficiency-current density, and(c) external quantum efficiency- (EQE-) current density of P1.

Table 5. Electroluminescence Data of P1^a

sample	$\lambda_{\rm El}~({\rm nm})$	LE (Cd/A)	V_{ONSET}	CIE coord (x,y)	EQE (%)
P1-5	530	0.100	6.2	0.34-0.56	0.032
P1-15	540	0.104	4.0	0.39-0.56	0.033
P1-25	545	0.129	3.6	0.42-0.55	0.042
P1-50	565	0.036	3.4	0.47-0.52	0.013

 ${}^{\alpha}\lambda_{\rm EP}$ main emission peak of the electroluminescense spectrum; LE, luminous efficiency; $V_{\rm ONSET}$, onset voltage; chromaticity coordinates according to the CIE 1931 diagram; and EQE, external quantum efficiency.

Moreover, maximum luminance of P1-5 was measured to be relatively higher compared to that of P1-15 and required considerably lower voltage to reach its maximum. The most significant and the systematic changes were found to be related to the on-set voltages, which decreased regularly with increasing DTT-S,S-dioxide ratio. It could be explained that DTT-S,Sdioxide lowers the energy barriers for better charge transport. On the other hand, P1-50 yielded the poorest performances of luminance and efficiencies, which could mean that electronhole balance in the active layer was negatively affected by alternating DTT-S,S-dioxide and fluorene units. A regular bathochromic shift on the electroluminescence spectra of the devices with the increasing content of DTT-S,S-dioxide of the copolymers was observed, which demonstrated that the initial green emission turned into yellow (see Supporting Information).

Regarding the device performances of polymers P2, the best efficiency was observed with polymer P2-5, even though its maximum luminous efficiency and the maximum luminance were obtained at relatively higher current densities and voltages compare with the outputs of the other P2 devices (Figure 7, Table 6). Although the luminous efficiency of the P2-5 was more than three times higher than that of P2-15 and P2-25, the differences between the EQE values were not that significant. P1 and P3 devices displayed similar trends in luminous and external quantum efficiencies. The onset voltages of P2-15, 25, and 50 were considerably lower than that of P2-5.

Table 6. Electroluminescence Data of $P2^{a}$

sample	$\lambda_{ m El} \ (nm)$	efficiency (Cd/A)	V _{ONSET}	CIE coord (<i>x</i> , <i>y</i>)	EQE (%)
P2-5	594	0.050	6.1	0.54-0.43	0.018
P2-15	612	0.014	3.6	0.60-0.39	0.011
P2-25	616	0.016	3.2	0.62-0.38	0.015
P2-50	630	0.006	4.5	0.61-0.38	0.006

 ${}^{\alpha}\lambda_{\rm EI}$ main emission peak of the electroluminescense spectrum, LE luminous efficiency, V_{ONSET} onset voltage, chromaticity coordinates according to the CIE 1931 diagram and EQE external quantum efficiency.

trend, observed with the polymers **P1**, a bathochromic shift with increasing content of DTT-*S*,*S*-dioxide took place with the polymers **P2**, the colors of which were orange-red (see Supporting Information).

The devices, fabricated using the copolymers P3, exhibited relatively lower luminance and efficiencies compared to that of the devices P1 and P2 (Figure 8, Table 7). Among the copolymers P3, while the best performance was achieved with P3-25, copolymer P3-50 had the poorest characteristics, as it was observed with copolymers P1. As distinct from both P1 and P2 devices, increasing DTT-*S*,*S*-dioxide content raises the on-set voltages of P3 devices. As expected, increasing DTT-*S*,*S*-dioxide content caused shift of electroluminescence spectra to higher wavelengths. Emission colors obtained from P3 varied from blue to green and yellow. As happened with the polymers P1 and P2, a bathocromic shift with the increasing content of DTT-*S*,*S*-dioxide was observed with the polymers P3 (see Supporting Information).

The colors of the three groups of the polymers **P1**, **P2**, and **P3**, demonstrated that while the most bathochromic shift was observed with the polymers **P2**, which had the longest extension with the thiophenes at the peripherals of DTT-*S*,*S*-dioxide, the polymers **P3** had the most hypsochromic shift, which had the least extension through the peripheral thiophenes of DTT-*S*,*S*-dioxide (Figure 9). A spread of colors from light blue to red through green and yellow was obtained.



Figure 7. (a) Luminance-voltage, (b) luminous efficiency-current density, and (c) EQE-current density of P2.



Figure 8. (a) Luminance-voltage, (b) luminous efficiency-current density, and (c) EQE-current density of P3.

Table 7. Electroluminescence Data of $P3^{a}$

sample	$\lambda_{ m El} \ (nm)$	efficiency (Cd/A)	V _{ONSET}	CIE coord (x,y)	EQE (%)
P3-5	441	0.006	5.5	0.22-0.25	0.004
P3-15	502	0.013	6.3	0.22-0.38	0.006
P3-25	556	0.042	6.5	0.40-0.52	0.015
P3-50	596	0.032	9.4	0.40-0.46	0.002

 ${}^{\alpha}\lambda_{\rm El}$ main emission peak of the electroluminescense spectrum, LE luminous efficiency, $V_{\rm ONSET}$ onset voltage, chromaticity coordinates according to the CIE 1931 diagram and EQE external quantum efficiency.



Figure 9. The x, y chromaticity coordinates of the polymers P1, P2, and P3, marked in CIE 1931 diagram.

Most interestingly, a light blue color just on the border of white region was obtained with **P3-5**.

CONCLUSIONS

In this work, copolymers of fluorene and dithienothiophene-*S*,*S*-dioxide (DTT-*S*,*S*-dioxide), having different ratios of DTT-*S*,*S*-dioxides (5, 15, 25 and 50%) were synthesized for finetuning the properties of the final materials such as their absorptions and fluorescence. The copolymers had three different groups (**P1**, **P2**, and **P3**) varying with the connection of fluorene to DTT-*S*,*S*-dioxide, where the copolymers **P1** and **P2** had direct connection of fluorene with DTT and connection through a thiophene unit, respectively. The connection between fluorene and DTT-*S*,*S*-dioxide in copolymers **P3** was provided through the phenyl moieties of the DTTs. Properties of the finely tuned copolymers were investigated by absorption and fluorescence spectroscopies, thermal gravity analyses, CV measurements and OLED applications. While the copolymers P1 and P2 had increasing bethochromic absorption and emission shifts with increasing contents of DTT-*S*,*S*-dioxide up to 447 and 472 nm (absorptions) and 558 and 592 nm (emissions) in solution, respectively, the copolymers P3 had increasing hypsochromic absorptions in solution and in solid state emissions with increasing contents of DTT-*S*,*S*-dioxide. Solid state emissions of the copolymers P3, having 5, 15, and 50% of DTT-*S*,*S*-dioxide displayed wide region of emission from 400 to 675 nm. OLEDs of the copolymers were fabricated, which had a spread of colors from light blue (border of white) to red, including green and yellow colors. In particular, the copolymers P2 (5–25%) and P3 had higher thermal stabilities with no weight loss up to 400 °C.

ASSOCIATED CONTENT

Supporting Information

¹³C and ¹H NMR, MS, and electroluminescence spectrat and device photographs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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DEDICATION

¹Dedicated to Prof Olgun Guven of Hacettepe University, Ankara, Turkey, on his retirement.

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