

# Poly(Fluorene-co-Thiophene)-Based Ionic Transition-Metal Complex Polymers for Solar Energy Harvesting and Storage Applications

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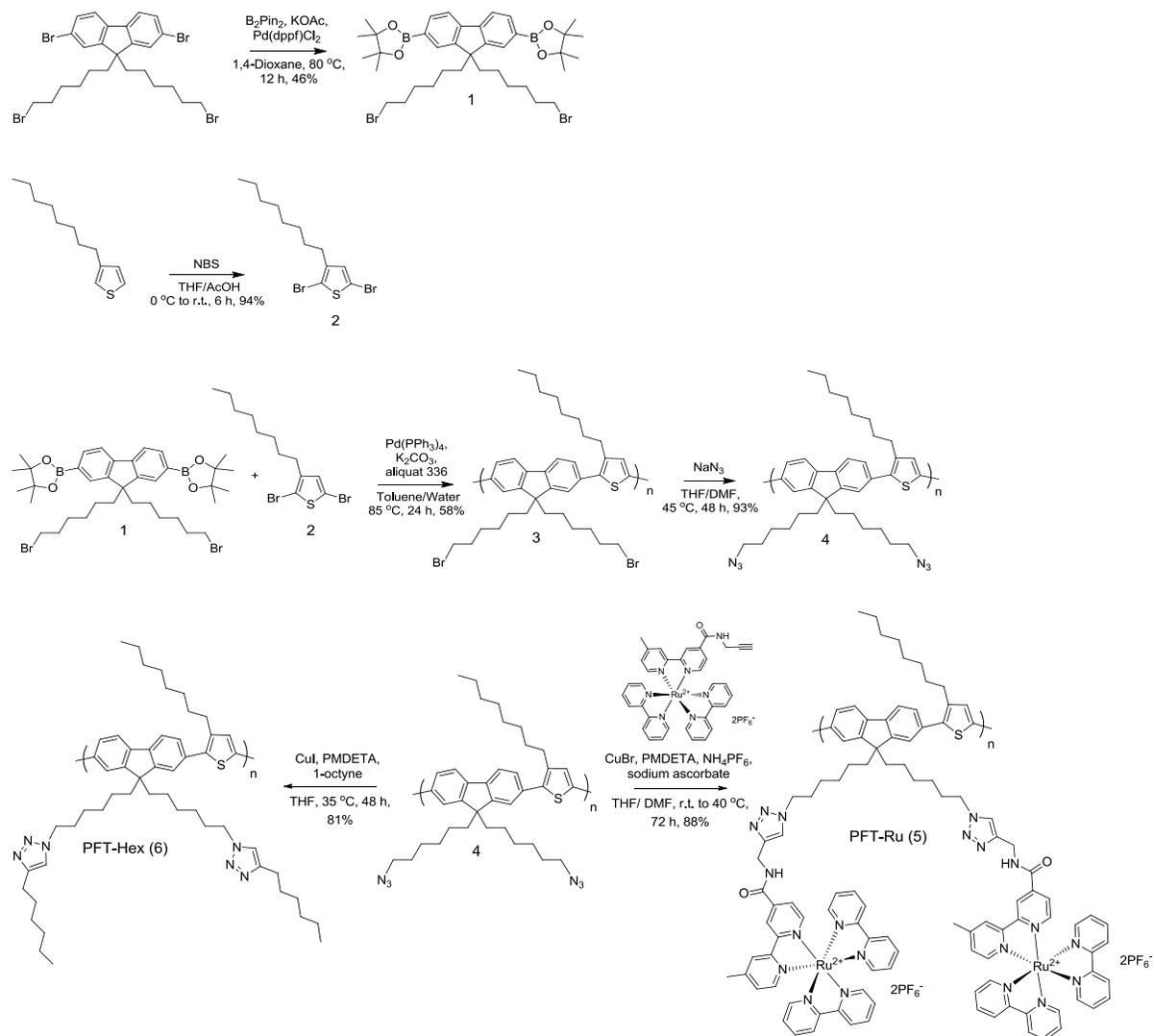
## *Supporting Information*

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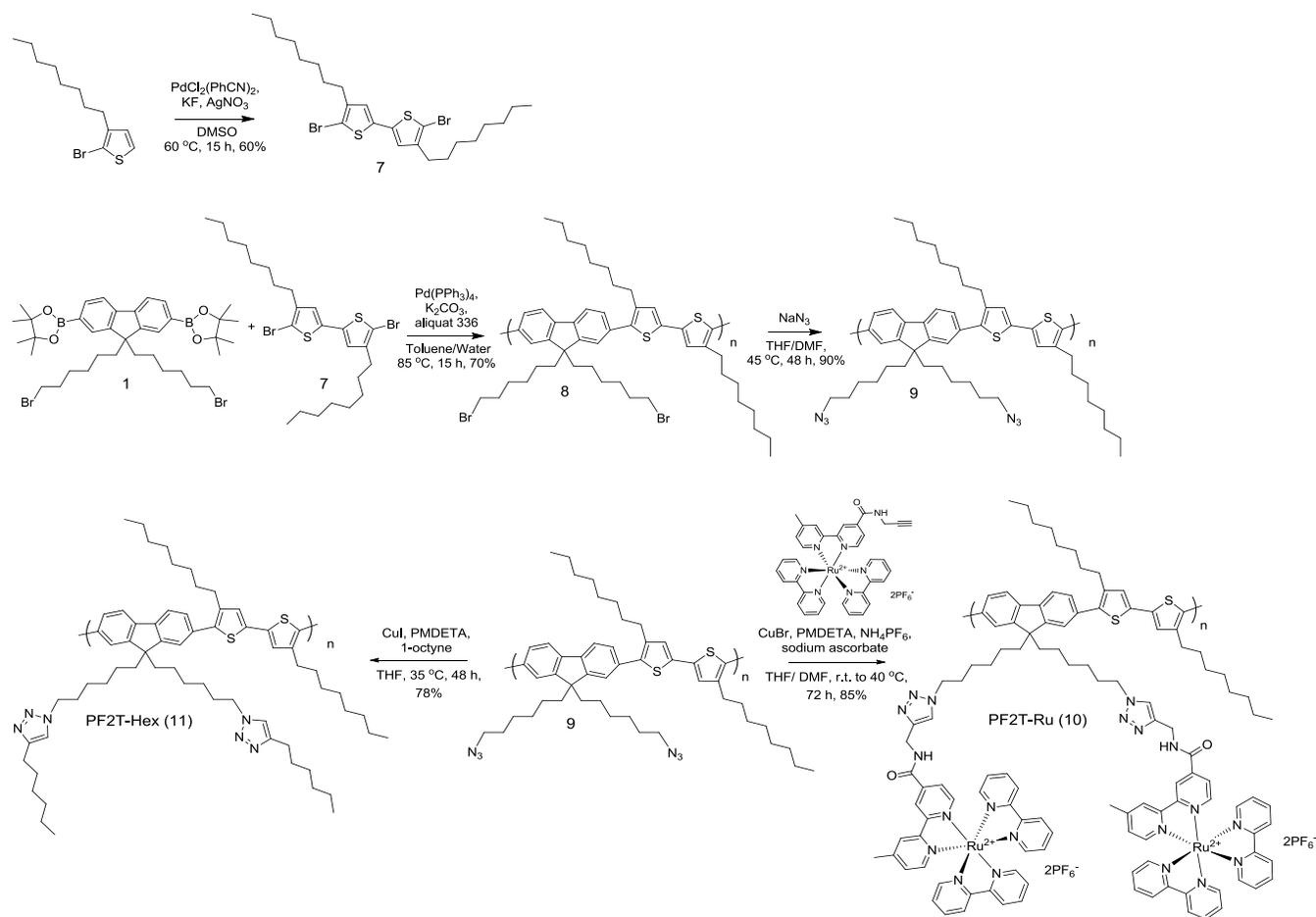
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## ADDITIONAL DATA

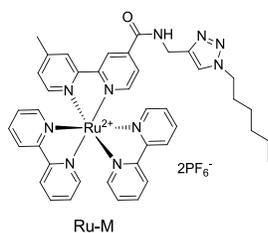
### Synthetic Schemes



**Scheme S1.** Synthetic routes to **PFT-Ru** (Polymer **5**) and **PFT-Hex** (Polymer **6**)



**Scheme S2.** Synthetic routes to **PF2T-Ru** (Polymer 10) and **PF2T-Hex** (Polymer 11)



**Scheme S3.** Structure of **Ru-M**<sup>1</sup>

## EXPERIMENTAL PROCEDURES

### *Materials*

The required materials, i.e. 4,4'-dimethyl-2,2'-bipyridyl, selenium dioxide, silver nitrate, potassium hydroxide, *N,N'*-dicyclohexylcarbodiimide (DCC), *N*-hydroxysuccinimide (NHS), sodium azide, potassium carbonate, 1,6-dibromohexane, 1-bromohexane, 1-octyne, tetrabutylammonium bromide, sodium ascorbate, 4-dimethyl-aminopyridine (DMAP), potassium acetate (KOAc), 3-octylthiophene, *N*-bromosuccinimide, bis(pinacolato)diboron, copper(I) bromide (CuBr, 99.999%), potassium fluoride (KF), ethylenediaminetetraacetic acid diammonium salt (ammonium EDTA) and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) were purchased from Sigma-Aldrich. Ammonium hexafluorophosphate (NH<sub>4</sub>PF<sub>6</sub>) and *cis*-bis-(2,2'-bipyridine)dichlororuthenium(II) dihydrate (Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O) were purchased from Alfa Aesar. Dichloro[1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloromethane adduct (Pd(dppf)Cl<sub>2</sub>), Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>) and dichlorobis(benzonitrile)palladium(II) (PdCl<sub>2</sub>(PhCN)<sub>2</sub>) was purchased from STREM Chemicals, Inc. All the chemicals were used as received unless otherwise indicated. Silica gel or alumina gel (reactivity grade I) were used for column chromatography. Dry solvents were obtained from a MBRAUN MB-SPS dry solvent system or purified using standard methods.<sup>2</sup> Solvents or liquid reagents for the use in a glove box were also degassed using at least three freeze-pump-thaw cycles.

**[Ru(2,2'-bipyridine)<sub>2</sub>(4'-methyl-2,2'-bipyridine-4-carbonyl propargyl amine)](PF<sub>6</sub>)<sub>2</sub><sup>1</sup>, Ru-M<sup>1</sup>, 2,7-dibromo-9,9-bis(6'-bromohexyl)fluorene<sup>3</sup>, and 2-Bromo-3-octylthiophene<sup>4,5</sup>** were prepared as described in the corresponding literature sources.

**9,9-Bis(6'-bromohexyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fluorene**

(**1**).<sup>6</sup> 2,7-dibromo-9,9-bis(6'-bromohexyl)fluorene<sup>3</sup> (3.00 g, 4.61 mmol), dry KOAc (3.23 g, 32.91 mmol) and bis(pinacolato)diboron (2.77 g, 10.91 mmol) were suspended in anhydrous 1,4-dioxane (50 mL) and degassed for 45 min. Under argon, Pd(dppf)Cl<sub>2</sub> (57.75 mg, 0.07 mmol) was added and the content of the flask was stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature, filtered, and the solvent from the filtrate was removed by rotary evaporation. The resulting residue was purified via silica gel column chromatography using ethyl acetate:hexanes (1:10 volume ratio) as the mobile phase. The solution obtained was evaporated to dryness, followed by recrystallization from ethanol/diethyl ether (diethyl ether was evaporated under a gentle nitrogen stream at room temperature to cause the recrystallization), to obtain **1** as white crystals in 46% (1.57 g) yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ (ppm): 0.49-0.63 (m, 4H); 0.98-1.22 (m, 8H); 1.40 (s, 24H); 1.63 (p, 4H, *J* = 7.1 Hz); 1.97-2.07 (m, 4H); 3.26 (t, 4H, *J* = 6.9 Hz); 7.70-7.77 (m, 4H); 7.82 (dd, 2H, *J*<sub>1</sub> = 7.4 Hz, *J*<sub>2</sub> = 1.4 Hz).

**2,5-Dibromo-3-octylthiophene** (**2**)<sup>7</sup> was synthesized using a modified literature procedure.<sup>8</sup> 3-Octylthiophene (2.00 g, 10.2 mmol), 20 mL of anhydrous THF, and 10 mL of glacial acetic acid were combined in a 100 mL three-neck round bottom flask and degassed by argon purging. The content of the flask was then cooled to 0 °C, and freshly recrystallized N-bromosuccinimide (NBS) (4.53 g of 25.5 mmol) was added to the solution under argon. The reaction mixture was protected from light, allowed to gradually warm to room temperature, and stirred at this temperature for 6 h. Excess THF was then removed by rotary evaporation, the resulting residue was diluted with water and extracted with diethyl ether. The organic phases were combined, dried over anhydrous MgSO<sub>4</sub>, and decolorizing carbon was added. The resulting suspension was filtered and the filtrate was evaporated to dryness. The obtained residue was

purified via silica column chromatography using hexanes as the mobile phase to afford **2** as colorless oil. Yield: 94% (3.40 g). The resulting compound was flushed with argon and stored at ~ 0 °C in the dark. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ (ppm): 0.89 (t, 3H, *J* = 6.7 Hz); 1.22-1.38 (m, 10H); 1.55 (p, 2H, *J* = 7.3 Hz); 2.51 (t, 2H, *J* = 7.6 Hz); 6.78 (s, 1H).

**Poly[(9,9-bis(6'-bromohexyl)fluorene)-co-(3-octylthiophene)] (3).** 2M potassium carbonate solution in deionized water was purged under argon at reflux for approximately one hour, cooled to room temperature and stored under argon. To a 100 mL 3-neck round bottom flask containing a magnetic stir bar, and outfitted with a glass stopper, condenser, and rubber septum, were added 9,9-bis(6'-bromohexyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fluorene (**1**) (441 mg, 0.593 mmol), 2,5-dibromo-3-octylthiophene (**2**) (210 mg, 0.593 mmol), and toluene (9 mL). This mixture was purged with argon for approximately 30 min and 5 mL of the 2M potassium carbonate solution was transferred to the reaction mixture. Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 0.030 mmol) was then added under argon. The flask was immersed in an 85 °C oil bath and stirred under a dynamic argon atmosphere for 24 h. The reaction mixture was then cooled to room temperature and precipitated into methanol/acetone/1N HBr mixture (70 mL/20 mL/20 mL). The precipitate was filtered over a nylon Osmonics™ membrane, washed with water and methanol. The solid obtained was redissolved in a small amount of THF and precipitated in 1:1 methanol:water solution (150 mL). The precipitate was collected by vacuum filtration, washed with water, methanol, acetone, as well as dried under vacuum. The resulting solid was then subjected to Soxhlet extraction with methanol (36 h) and chloroform (24 h). The chloroform soluble fraction was then concentrated, precipitated into methanol, filtered and dried. The product was isolated as a light yellow solid in 58% (235 mg) yield. GPC (versus polystyrene in THF): *M<sub>n</sub>* = 15.6 kDa, PDI = 2.9. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ (ppm): 0.58-2.22 (m, 35H);

2.76 (bs, 2H); 3.30 (t, 4H,  $J = 6.3$  Hz); 7.30-7.88 (m, 7H). Anal. calculated for  $C_{37}H_{48}Br_2S$ : C, 64.91; H, 7.07; N, 0.00; found: C, 65.89; H, 7.21; N, 0.00.

**Poly[(9,9-bis(6'-azidohexyl)fluorene)-co-(3-octylthiophene)] (4).** To a solution of **3** (110 mg, 0.161 mmol) in 100 mL of dry THF and 50 mL of dry DMF, at room temperature, sodium azide (104 mg, 1.607 mmol) was added. (*Caution! Sodium azide is highly toxic and presents a severe explosion risk when shocked, heated, or treated with acid.*) The mixture obtained was stirred for 48 h at 45 °C under an argon atmosphere in the dark. The reaction mixture was cooled to room temperature and the excess THF was evaporated under vacuum. To the resulting suspension, methanol (100 mL) was added; the precipitate was collected by vacuum filtration, and washed with methanol, water and acetone. Due to the increased sensitivity to azide cross-linking,<sup>9</sup> polymer **4** was immediately used for the next synthetic steps without further purification. Additionally, this reaction and the work-up of polymer **4** were carried out with minimal exposure to light. Yield of light yellow solid: 91 mg, 93%. <sup>1</sup>H NMR (300 MHz,  $CDCl_3$ ),  $\delta$  (ppm): 0.56-2.25 (m, 35H); 2.75 (bs, 2H); 3.14 (m, 4H); 7.30-7.88 (m, 7H).

**PFT-Ru (5).** Polymer **4** (25.0 mg, 0.041 mmol),  $[Ru(2,2'$ -bipyridine)<sub>2</sub>(4'-methyl-2,2'-bipyridine-4-carbonyl propargyl amine)](PF<sub>6</sub>)<sub>2</sub> (109.8 mg, 0.115 mmol), PMDETA (19.9 mg, 0.115 mmol), sodium ascorbate (11.5 mg, 0.058 mmol), NH<sub>4</sub>PF<sub>6</sub> (ca. 1 g), THF (30 mL) and DMF (15 mL) were combined in a round bottom flask and degassed for 30 min (argon purging). After the addition of CuBr (16.5 mg, 0.115 mmol), the content of the flask was further degassed for 10 more min and stirred at room temperature for 48 h under an argon atmosphere. Under argon, additional  $[Ru(2,2'$ -bipyridine)<sub>2</sub>(4'-methyl-2,2'-bipyridine-4-carbonyl propargyl amine)](PF<sub>6</sub>)<sub>2</sub> (54.9 mg, 0.058 mmol), PMDETA (10.0 mg, 0.058 mmol), sodium ascorbate (5.8 mg, 0.029 mmol) and CuBr (8.3 mg, 0.058 mmol) were added to the reaction mixture and the

solution was further stirred for 24 h at 40 °C upon slow argon purging allowing for slow gradual THF evaporation. After the completion of the reaction (FT-IR control: azide signal at ca. 2095  $\text{cm}^{-1}$  disappeared), the reaction mixture was subjected to a gentle nitrogen stream to evaporate the leftover THF and the remaining solution was precipitated into water containing ca. 0.5 g of  $\text{NH}_4\text{PF}_6$ . The resulting precipitate was collected by vacuum filtration and washed with water, methanol and THF. The solid obtained was dissolved in a small amount of acetonitrile; the resulting solution was filtered through a 0.45  $\mu\text{m}$  Whatman syringe filter to remove an insoluble impurity and evaporated to dryness. The remaining residue was then redissolved in 20 mL of HPLC grade acetone containing ca. 0.5 mL PMDETA and ca. 0.2 g  $\text{NH}_4\text{PF}_6$ , stirred for 0.5 h, precipitated upon addition of deionized water (ca. 50 mL) and collected by vacuum filtration and this process was repeated three times. The procedure was repeated two more times (excluding PMDETA addition and reducing the stirring time to 20 min), and the brown precipitate was collected by filtration, washed with water, methanol and diethyl ether, and dried under vacuum. Yield: 91 mg, 88%.  $^1\text{H}$  NMR (300 MHz, acetonitrile- $\text{d}_3$ ),  $\delta$  (ppm): 0.47-2.23 (m, 35H); 2.47 (s, 6H); 2.72 (bs, 2H); 4.13 (bs, 4H); 4.54 (bs, 4H); 7.16-8.88 (m, 55H). Anal. calculated for  $\text{C}_{107}\text{H}_{106}\text{F}_{24}\text{N}_{20}\text{O}_2\text{P}_4\text{SRu}_2$ : C, 51.03; H, 4.24; N, 11.12; found: C, 51.64; H, 4.75; N, 10.62.

**PFT-Hex (6).** To a solution of **4** (50 mg, 0.082 mmol) in 50 mL of dry THF, 36 mg of 1-octyne (0.328 mmol) and 43 mg (0.246 mmol) of PMDETA were added. The reaction mixture was degassed for 30 min followed by the addition of 24 mg (0.164 mmol) of CuBr. The reaction mixture was stirred at 35 °C for 48 h under argon atmosphere, cooled down to room temperature, and poured into 200 mL of diethyl ether. The resulting precipitate was collected by vacuum filtration and dried. To remove trace copper impurities, a solution of **6** in 10 mL of DCM was stirred vigorously with 10% aqueous solution of ammonium EDTA overnight. The organic

fraction was collected and evaporated to dryness by rotary evaporation. The remaining residue was redissolved in THF, and precipitated into methanol/water (1:1). The precipitate was collected by filtration, dried. Yield of light yellow solid: 55 mg, 81%. GPC (versus polystyrene in THF):  $M_n = 25.8$  kDa, PDI = 1.4.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 0.55-2.20 (m, 57H); 3.65 (t, 4H,  $J = 7.5$  Hz); 2.74 (bs, 2H); 4.16 (bs, 4H); 7.14 (bs, 2H); 7.30-7.85 (m, 7H). Anal. calculated for  $\text{C}_{53}\text{H}_{76}\text{N}_6\text{S}$ : C, 76.76; H, 9.24; N, 10.13; found: C, 75.90; H, 9.43; N, 9.19.

**5,5'-Dibromo-4,4'-dioctyl-2,2'-bithiophene (7)**<sup>10</sup> was synthesized via a modified literature procedure.<sup>4</sup> 2-Bromo-3-octylthiophene (2.00 g, 7.27 mmol),  $\text{PdCl}_2(\text{PhCN})_2$  (0.032 g, 0.083 mmol) and KF (0.94 g, 16.18 mmol) were dissolved in 40 ml of anhydrous DMSO and degassed by argon purging. 2.75 g (16.18 mmol) of  $\text{AgNO}_3$  were added to the flask under an inert atmosphere, and the resulting mixture was stirred at 60 °C for 3 hours in the dark. The content of the flask was cooled to room temperature, and additional  $\text{AgNO}_3$  (2.75 g, 16.18 mmol) and KF (0.94 g, 16.18 mmol) were added to the reaction mixture. The resulting suspension was then stirred at 60 °C for 12 hours, cooled down to room temperature and KOH was added to neutralize HF that could have potentially formed during the course of the reaction. The suspension obtained was then filtered over a celite pad, diluted with water and extracted with diethyl ether. The organic fractions were combined, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and the filtrate was concentrated. The obtained solution was evaporated to dryness, and the obtained residue was purified via a silica plug using hexanes as the mobile phase. The resulting solution was evaporated to dryness and purified by HPLC using C18 stationary phase column and acetonitrile:tetrahydrofuran in 3:1 volume ratio as an eluent mixture. The desired product was obtained in 60% yield (2.40 g) as light yellow oil which solidified upon standing.  $^1\text{H}$  NMR (300

MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 0.90 (t, 6H,  $J = 6.8$  Hz), 1.25-1.40 (m, 20H), 1.52-1.65 (m, 4H), 2.53 (t, 4H,  $J = 7.7$  Hz), 6.78 (s, 2H).

**Poly[(9,9-bis(6'-bromohexyl)fluorene)-co-(4,4'-dioctyl-2,2'-bithiophene)]** (**8**) was synthesized by employing the same procedure as for the synthesis of **3** using 9,9-bis(6'-bromohexyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fluorene (**1**) (418 mg, 0.562 mmol) and 5,5'-dibromo-4,4'-dioctyl-2,2'-bithiophene (**7**) (308 mg, 0.562 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (32 mg, 0.028 mmol). The product was isolated as a yellow solid in 70% (346 mg) yield. GPC (versus polystyrene in THF):  $M_n = 13.1$  kDa, PDI = 2.3. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 0.58-2.20 (m, 50H); 2.72 (bs, 4H); 3.31 (t, 4H,  $J = 6.6$  Hz); 7.14 (bs, 2H); 7.35-7.54 (m, 4H), 7.68-7.82 (m, 2H). Anal. calculated for C<sub>49</sub>H<sub>66</sub>Br<sub>2</sub>S<sub>2</sub>: C, 66.95; H, 7.57; N, 0.00; found: C, 65.90; H, 7.04; N, 0.00.

**Poly[(9,9-bis(6'-azidohexyl)fluorene)-co-(4,4'-dioctyl-2,2'-bithiophene)]** (**9**) was synthesized by employing the same procedure as for **4** using polymer **8** (142 mg, 0.162 mmol) and sodium azide (105 mg, 1.615 mmol). Yield of the bright yellow solid: 117 g, 90%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 0.62-2.18 (m, 50H); 2.72 (bs, 4H); 3.16 (t, 4H,  $J = 7.0$  Hz); 7.13 (bs, 2H); 7.40-7.52 (m, 4H), 7.73-7.81 (m, 2H).

**PF2T-Ru** (**10**) was obtained by employing the same procedure as for the synthesis of polymer **5** using polymer **9** (25.0 mg, 0.031 mmol), [Ru(2,2'-bipyridine)<sub>2</sub>(4'-methyl-2,2'-bipyridine-4-carbonyl propargyl amine)](PF<sub>6</sub>)<sub>2</sub> (83.1 mg, 0.087 mmol), PMDETA (15.1 mg, 0.087 mmol), sodium ascorbate (8.7 mg, 0.044 mmol), NH<sub>4</sub>PF<sub>6</sub> (ca. 1 g) and CuBr (12.5 mg, 0.087 mmol). The second addition of reagents contained complex [Ru(2,2'-bipyridine)<sub>2</sub>(4'-methyl-2,2'-bipyridine-4-carbonyl propargyl amine)](PF<sub>6</sub>)<sub>2</sub> (42.0 mg, 0.044 mmol), PMDETA (7.6 mg, 0.044 mmol), sodium ascorbate (4.4 mg, 0.022 mmol) and CuBr (6.3 mg, 0.044 mmol).

Yield of the orange-red solid: 72 mg, 85%.  $^1\text{H}$  NMR (300 MHz, acetonitrile- $d_3$ ),  $\delta$  (ppm): 0.49-2.22 (m, 50H); 2.49 (s, 6H); 2.67 (bs, 4H); 4.15 (m, 4H); 4.57 (m, 4H); 7.05-8.86 (m, 56H). Anal. calculated for  $\text{C}_{119}\text{H}_{124}\text{F}_{24}\text{N}_{20}\text{O}_2\text{P}_4\text{S}_2\text{Ru}_2$ : C, 52.69; H, 4.61; N, 10.33; found: C, 53.36; H, 4.92; N, 9.60.

**PF2T-Hex (11)** was obtained by employing the same procedure as for the synthesis of polymer **6** using polymer **9** (50 mg, 0.062 mmol), 1-octyne (27 mg, 0.248 mmol), PMDETA (32 mg, 0.186 mmol) and CuBr (18 mg, 0.124 mmol). Yield of yellow solid: 50 mg, 78%. GPC (versus polystyrene in THF):  $M_n = 13.3$  kDa, PDI = 2.0.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 0.55-2.17 (m, 72H); 2.59-2.78 (m, 8H); 4.18 (t, 4H,  $J = 7.0$  Hz); 7.13 (bs, 4H); 7.35-7.55 (m, 4H), 7.69-7.84 (m, 2H). Anal. calculated for  $\text{C}_{65}\text{H}_{94}\text{N}_6\text{S}_2$ : C, 76.27; H, 9.26; N, 8.21; found: C, 75.54; H, 9.22; N, 7.62.

### *Instrumentation and Measurements*

**Materials Characterization.** NMR spectra were measured on a Gemini-300 FT-NMR, a VXR 300 FT-NMR, or a Mercury-300 FT-NMR. High resolution mass spectrometry was performed on a Bruker APEX II 4.7 T Fourier Transform Ion Cyclone Resonance mass spectrometer (Bruker Daltonics, Billerica, MA) or a Finnigan LCQ - Quadrupole Ion Trap (Thermo Finnigan, San Jose, CA). The FT-IR spectra were obtained with a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analysis was performed on an Eager 200. Gel permeation chromatography (GPC) was performed using a Waters Associates GPCV2000 liquid chromatography system with its internal differential refractive index detector (DRI) at 40 °C, using two Waters Styragel HR-5E columns (10  $\mu\text{m}$  PD, 7.8 mm i.d., 300 mm length) with HPLC grade THF as the mobile phase at a flow rate of 1.0  $\text{mL min}^{-1}$ . Injections were made at 0.05 -

0.07% w/v sample concentration using a 220.5  $\mu\text{L}$  injection volume. Retention times were calibrated against narrow molecular weight polystyrene standards (Polymer Laboratories; Amherst, MA). High pressure liquid chromatography (HPLC) was performed on a Hitachi EZ chrome system, using a Lachrom ultra 4.6 mm X 150 mm C18 (TMS endcapped, 5  $\mu\text{m}$  particle size) column. Preparative HPLC was carried out using a Lachrom Ultra 21.2 mm X 250 mm C18 (TMS endcapped, 10  $\mu\text{m}$  particle size) column.

**Electrochemistry.** Electrochemical studies were performed using a single-compartment three-electrode cell with a platinum flag as the counter electrode, a non-aqueous  $\text{Ag}/\text{Ag}^+$  reference electrode (calibrated versus ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) standard redox couple using a 5 mM solution of ferrocene in 0.1 M  $\text{TBAPF}_6$ /acetonitrile), and a platinum button (0.02  $\text{cm}^2$ ) as the working electrode. Cyclic voltammetry and differential pulse voltammetry measurements were carried out in 0.1 M  $\text{TBAPF}_6$  acetonitrile, dichloromethane or tetrahydrofuran (THF) electrolyte solutions with the analyte concentration of *ca.* 1-3 mM. All potentials are reported vs.  $\text{Fc}/\text{Fc}^+$ . An EG&G Princeton Applied Research model 273A potentiostat/galvanostat was operated under the control of Corrware<sup>®</sup> II software from Scribner and Associates. Electrochemical measurements were performed in an argon-filled glove box (Vacuum Atmospheres).

***In Situ* Spectroelectrochemistry.**<sup>11</sup> Sub-second spectroelectrochemical data acquisition was performed on an Ocean Optics USB2000+ spectrophotometer detector and associated Ocean Optics DH-2000-BAL fiber-optic light source. The detector was placed, along with cuvette holders, in an enclosure designed to eliminate extraneous light. Spectral data were collected upon linear sweep voltammetry scans of the polymer films, spin-coated or drop-cast on indium tin oxide (ITO)-coated glass slides ( $7 \times 50 \times 0.7$  mm, sheet resistance,  $R_s = 8\text{--}12 \Omega/\text{cm}^2$ , purchased

from Delta Technologies, Ltd.) in 1 cm quartz cuvette cells under similar conditions to those used for the electrochemical measurements. The experiments were performed in 0.1 M TBAPF<sub>6</sub> tetrahydrofuran or acetonitrile electrolyte solutions using an ITO/glass slide as the working electrode, a silver wire pseudoreference electrode (calibrated vs. Fc/Fc<sup>+</sup> standard redox couple), and a platinum wire as the counter electrode. All samples were prepared in an argon filled drybox and the resulting cuvettes were sealed with parafilm and teflon tape prior to exposure to ambient atmosphere. The absorption spectra obtained were smoothed using OriginPro 7.5 software Adjacent Averaging function.

**PFT-Ru** (polymer **5**) and **PF2T-Ru** (polymer **10**) films were drop-casted on ITO/glass slides from acetonitrile solutions, whereas **PFT-Hex** (polymer **6**) and **PF2T-Hex** (polymer **11**) films were processed in a similar fashion from THF solutions.

**Ground State Absorption.** UV-Visible spectra were recorded on an Agilent 8543 Diode Array Spectrophotometer interfaced to a computer using a 1.0 cm quartz cuvette. UV-Visible spectra were recorded on all samples before and after excited state measurements to ensure that samples did not undergo photodecomposition.

**Steady State Emission.** Emission spectra were measured on a Photon Technology International Quantamaster™ spectrofluorometer using a 1.0 cm quartz cuvette. A 75W continuous xenon arc lamp was used as the excitation source. The emitting light was collected at 90° to the excitation beam and detected by a Multi-mode 814 photomultiplier tube (PMT) in photon counting mode (digital).

**Time-Resolved Emission.** The lifetimes of excited state in the picosecond scale were measured by a streak camera setup. The excitation pulse was generated from a mode-locked Ti:Sapphire laser (Spectra Physics, Tsunami). The fundamental had an 80 fs pulse duration at an

80 MHz repetition rate, tunable between 720 and 850 nm. The laser output was sent through an acousto-optic modulator pulse picker and frequency doubler to obtain 370-450 nm pulses at repetition rate at least 5 times the natural lifetime of the sample. Fluorescence was collected 90° to the excitation beam and focused into the entrance slit of a C11119-01 spectrograph, which was coupled to a Hamamatsu C10627 streak camera. The instrument response function was ~15 ps.

The lifetimes of the excited state in the ns to  $\mu$ s range (*i.e.* Ru polypyridyl complexes) were measured by using the time-correlated single-photon counting (TCSPC) technique on the FLS920 system. The Edinburgh EPL 445 nm picosecond pulsed diode laser (74.4 ps pulse width) was used as the excitation source, and R2658P photomultiplier tube as the detector. The Instrument Response Function (IRF) of the photomultipliers, measured with the short pulse laser excitation is 200 ps in the visible range.

**Transient Absorption Measurements.** Transient absorption measurements were conducted by using a pump-probe technique. The pump and probe pulses were generated from a Ti:Sapphire chirped pulse amplification (CPA) laser system (Clark-MXR CPA-2001). The fundamental pulses were centered at 775 nm (~ 150 fs FWHM) at a 1 kHz repetition rate. The 388 nm pump pulse was generated by doubling the fundamental output at 775 nm through a 2 mm BBO crystal. The probe pulse was produced from continuum generation by focusing ~ 3 mW of the fundamental into a translating CaF<sub>2</sub> window. Delay between pump and probe pulses was controlled by a computer controlled mechanical delay stage. The pump beam was focused into the sample using a 300 mm lens and the probe beams is focused with a 250 mm spherical aluminum mirror and overlapped with the pump pulse in the sample. The transmitted probe pulse was coupled into multichannel spectrometer with a CMOS sensor with 1.5 nm intrinsic resolution. Spectra were collected on a shot-by-shot (1 kHz) basis over the range of 300 to 700

nm. The instrument sensitivity was up to 0.1 mOD. The kinetic window ranges from 250 fs – approximately 1.5 ns.

The probe pulse for sub-nanosecond measurements was generated by continuum generation from a photonic crystal fiber and detected by a fiber optic coupled multichannel spectrometer with a CMOS sensor. The kinetic window ranges from 500 ps – 400  $\mu$ s, and the time resolution of the instrument is around 500 ps dictated by the width of the probe pulse and the timing electronics.

## REFERENCES

1. Wang, L.; Puodziukynaite, E.; Vary, R. P.; Grumstrup, E. M.; Walczak, R. M.; Zolotarskaya, O. Y.; Schanze, K. S.; Reynolds, J. R.; Papanikolas, J. M., Competition between Ultrafast Energy Flow and Electron Transfer in a Ru(II)-Loaded Polyfluorene Light-Harvesting Polymer. *J. Phys. Chem. Lett.* **2012**, 3, (17), 2453-2457.
2. Armarego, W. L. F.; Chai, C., *Purification of Laboratory Chemicals, 5th Edition*. Butterworth-Heinemann: 2003; p 608 pp.
3. Lu, H.-H.; Ma, Y.-S.; Yang, N.-J.; Lin, G.-H.; Wu, Y.-C.; Chen, S.-A., Creating a Pseudometallic State of K<sup>+</sup> by Intercalation into 18-Crown-6 Grafted on Polyfluorene as Electron Injection Layer for High Performance PLEDs with Oxygen- and Moisture-Stable Al Cathode. *J. Am. Chem. Soc.* 133, (25), 9634-9637.
4. Takahashi, M.; Masui, K.; Sekiguchi, H.; Kobayashi, N.; Mori, A.; Funahashi, M.; Tamaoki, N., Palladium-Catalyzed C-H Homocoupling of Bromothiophene Derivatives and Synthetic Application to Well-Defined Oligothiophenes. *J. Am. Chem. Soc.* **2006**, 128, (33), 10930-10933.

5. Querner, C.; Benedetto, A.; Demadrille, R.; Rannou, P.; Reiss, P., Carbodithioate-Containing Oligo- and Polythiophenes for Nanocrystals' Surface Functionalization. *Chem. Mater.* **2006**, 18, (20), 4817-4826.
6. Pu, K.-Y.; Fang, Z.; Liu, B., Effect of Charge Density on Energy-Transfer Properties of Cationic Conjugated Polymers. *Adv. Funct. Mater.* **2008**, 18, (8), 1321-1328.
7. Dilien, H.; Palmaerts, A.; Lenes, M.; de, B. B.; Blom, P.; Cleij, T. J.; Lutsen, L.; Vanderzande, D., A deeper Insight into the Dithiocarbamate Precursor Route: Synthesis of Soluble Poly(thienylene vinylene) Derivatives for Photovoltaic Applications. *Macromolecules* **2010**, 43, (24), 10231-10240.
8. Wu, I. C.; Lai, C.-H.; Chen, D.-Y.; Shih, C.-W.; Wei, C.-Y.; Ko, B.-T.; Ting, C.; Chou, P.-T., Cu(I) Chelated Poly-Alkoxythiophene Enhancing Photovoltaic Device Composed of a P3HT/PCBM Heterojunction System. *J. Mater. Chem.* **2008**, 18, (36), 4297-4303.
9. Kim, H. J.; Han, A. R.; Cho, C.-H.; Kang, H.; Cho, H.-H.; Lee, M. Y.; Frechet, J. M. J.; Oh, J. H.; Kim, B. J., Solvent-Resistant Organic Transistors and Thermally Stable Organic Photovoltaics Based on Cross-linkable Conjugated Polymers. *Chem. Mater.* **2012**, 24, (1), 215-221.
10. Zrig, S.; Koeckelberghs, G.; Verbiest, T.; Andrioletti, B.; Rose, E.; Persoons, A.; Asselberghs, I.; Clays, K., L-Type Regioregular Oligothiophenes: Synthesis and Second-Order NLO Properties. *J. Org. Chem.* **2007**, 72, (15), 5855-5858.
11. Liu, D. Y.; Chilton, A. D.; Shi, P.; Craig, M. R.; Miles, S. D.; Dyer, A. L.; Ballarotto, V. W.; Reynolds, J. R., In Situ Spectroscopic Analysis of Sub-Second Switching Polymer Electrochromes. *Adv. Funct. Mater.* **2011**, 21, (23), 4535-4542.