Synthesis, structure, and optoelectronic properties of phosphafluorene copolymers

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Characterization: NMR spectra were collected on a Varian Mercury Plus 400 spectrometer with chloroform-*d* or DMSO-*d* as the solvent and tetramethylsilane as the internal standard. MALDI-TOF experiments were carried out using a Shimadzu AXIMA-CFRTM plus time-of-flight mass spectrometer (Kratos Analytical, Manchester, U.K.). Elemental analysis was performed on a CHNS-O (Elementar Co.). The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the polymers was measured by gel permeation chromatography (GPC) using polystyrene as standards. Thermogravimetric analyses (TGA) were conducted on a Shimadzu thermogravimetry and differential thermal analysis DTG-60H at a heating rate of 10 °C/min and a nitrogen flow rate of 70 mL/min. Differential scanning calorimetry (DSC) was run on a DSC-60 TA Shimadzu thermal analyst system. UV-Vis spectra were recorded on a Shimadzu 3150 PC Spectrophotometer. The concentrations of copolymer solution (in THF) were adjusted to about 0.01 mg/mL or less; The solid

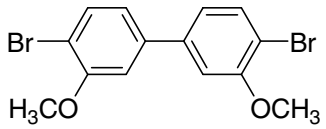
films were prepared via natural drying of the above solution on a quartz substrate. Fluorescence measurement was carried out on a Shimadzu RF-5301 PC spectrofluorophotometer with a xenon lamp as a light source. The highest occupied molecular obital (HOMO) and the lowest unccupied molecular obital (LUMO) and the energy gap between them (E_g) were measured by Cyclic voltammetry (CV). The CV measurements were performed at room temperature on an Ecochemie's Autolab system in a typical three-electrode cell with a working electrode (glass carbon), a reference electrode (Ag/Ag^+, referenced against ferrocene/ferrocenium (FOC)), and a count electrode (Pt wire) under a nitrogen atmosphere in a solution of Bu_4NPF_6 (0.10 M) in acetonitrile at a sweeping rate of 100 mV/s. The HOMO/LUMO energy levels of the material are estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum): HOMO/LUMO = $-[E_{onset} - (-0.047)] - 4.8$ eV, where the value of –0.047 V is for FOC vs Ag/Ag^+ and E_{onset} is the onset potential.

Light-emitting diode devices were fabricated on pre-patterned indium-tin oxide (ITO) with sheet resistance 10-20 Ω/□. The substrate was ultrasonic cleaned with acetone, detergent, deionized water, and 2-propanol. Oxygen plasma treatment was made for 4 min as the final step just before film coating. Onto the ITO glass was spin-coated a layer of polyethylenedioxythiophene-polystyrene sulfonic acid (PEDOT:PSS) film with thickness of 40 nm from its aqueous dispersion. PEDOT:PSS film was dried at 80 °C for 3 h in the vacuum oven. The solution of the polymer was prepared under nitrogen atmosphere and spin-coated on to PEDOT:PSS layer. Typical thickness of the emitting layer was 80 nm. Then a thin layer of barium as an electron

injection cathode and the subsequent 130 nm thick aluminum protection layers were thermally deposited by vacuum evaporation through a mask at a base pressure below 2 × 10^{-4} Pa. The cathode area defines the active area of the device. The typical active area of the devices in this study is 0.15 cm^2. The device performance tests were carried out within a glovebox under nitrogen atmosphere. Current-voltage (I-V) characteristics were recorded with a Keithley 236 source meter. Electroluminescent (EL) spectra were obtained by Oriel Instaspec IV CCD spectrograph. Luminance was measured by a PR 705 photometer (Photo Research). The external quantum efficiencies were determined by a Si photodiode with calibration in an integrating sphere (IS080, Labsphere).

Materials: Commercially available chemicals (Acros) were used without further purification. 2,7-Dibromo-3,6-dimethoxyl-9-phenyl-9-phosphafluorene (1), 2,7-Dibromo-3,6-dimethoxyl-9-butyl-9-phosphafluorene oxide (2), 9,9-dioctylfluorene-2,7-dibromide (3), and 9,9-dioctylfluorene-2,7-bis(trimethylene boronate) (4) were synthesized according to literature procedures [1,2].

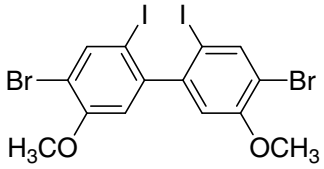
4,4'-dibromo-3,3'-dimethoxylbiphenyl



o-Dianisidine (5.0 g) was dissolved in a hot mixture of 40□ hydrobromic acid (20 ml), water (80 ml) and acetonitrile (80 ml). The solution was cooled to 0 °C and sodium nitrite (3.6 g) in cold water (7 ml) was added with stirring, the temperature being kept below 10 °C. Cuprous bromide (6.5 g) in hydrobromic acid (80 ml) was added to the cold diazonium compound with vigorous stirring, and after the mixture warmed up to the room temperature it was heated until the evolution of nitrogen ceased. The precipitate was extracted with

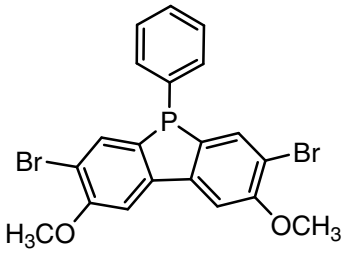
chloroform, washed with water, chromatographed on alumina, and dried. Evaporation of the extract gave the crude product of 7.5 g (yield > 99%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ7.60 (d, 2H, ^{3}J =7.6 Hz); δ7.04 (d, 2H, ^{4}J =1.6 Hz); δ7.03 (dd, 2H, ^{3}J =8.0 Hz, ^{4}J =2.0 Hz); δ3.97 (s, 6H). Anal. Calcd. for $C_{14}H_{12}Br_2O_2$: C, 45.20; H, 3.25. Found: C, 45.43; H, 3.327.

4,4'-dibromo-6,6'-diiodo-3,3'-dimethoxylbiphenyl



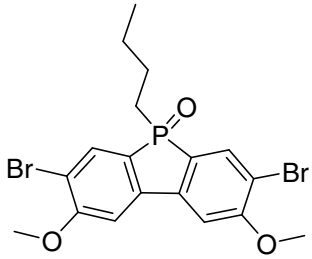
A mixture of 4,4'-dibromo-3,3'-dimethoxylbiphenyl (7.5g, 20 mmol), KIO_3 (1.9 g, 8.8 mmol), I_2 (5.6 g, 22 mmol), and 20% H_2SO_4 (15 mL) in AcOH (150 mL) was heated at 80 °C overnight. When the reaction mixture was cooled to room temperature, water (200 mL) was added. The precipitate was collected, dissolved in chloroform and washed with aqueous $Na_2S_2O_3$ and brine, and dried over magnesium sulfate. After the solvent was evaporated, the product was purified through silica gel chromatography and recrystallized twice from ethanol to afford 11.6 g (yield: 93%) colorless crystal. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ8.05 (s, 2H); δ6.72 (s, 2H); δ3.88 (s, 6H). Anal. Calcd. for $C_{14}H_{10}Br_2I_2O_2$: C, 26.95; H, 1.62. Found: C, 26.28; H, 1.646.

2,7-Dibromo-3,6-dimethoxyl-9-phenyl-9-phosphafluorene (7)



Yield: 54%. ^{1}H NMR (DMSO, 400 MHz, ppm): δ7.98 (s, 2H); δ7.95 (d, 2H, $^{3}J_{H,P}$ = 4.8 Hz); δ7.32-7.21 (b, 5H); δ4.01 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ56.72; δ104.67; δ112.50; δ129.08; δ129.99; δ131.30; δ133.06; δ135.01; δ136.40; δ143.90; δ157.03. GC-MS (EI-*m/z*): 478 (M^+). MALDI-TOF, *m/z*: 875.2, 795.3, 555.2, 478.0. Anal. Calcd. for $C_{20}H_{15}Br_2O_2P$: C, 50.24; H, 3.16. Found: C, 49.86; H, 3.172.

2,7-Dibromo-3,6-dimethoxyl-9-butyl-9-phosphafluorene oxide



Yield: 24%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ7.88 (d, 2H, $^{3}J_{H,P}$ = 9.2 Hz); δ7.14 (d, 2H, $^{4}J_{H,P}$ = 2.8 Hz); δ4.04 (s, 6H); δ2.05-2.00 (b, 2H); δ1.23-1.13 (b, 4H); δ0.84 (t, 3H, ^{3}J = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ13.71; δ24.07 ($^{2}J_{CP}$ = 17.0 Hz); δ24.42 ($^{3}J_{CP}$ = 3.7 Hz); δ30.54 ($^{1}J_{CP}$ = 71.7 Hz); δ56.82; δ104.59 ($^{3}J_{CP}$ = 11.2 Hz); δ113.56 ($^{3}J_{CP}$ = 14.4 Hz); δ125.71 ($^{1}J_{CP}$ = 102.2 Hz); δ134.04 ($^{2}J_{CP}$ = 11.7 Hz); δ141.97 ($^{2}J_{CP}$ = 20.0 Hz); δ160.04 ($^{4}J_{CP}$ = 0.9 Hz). MALDI-TOF *m/z*: 473.0, 471.0. Anal. Calcd. for $C_{18}H_{19}B_{r2}O_3P$: C, 45.60; H, 4.04. Found: C, 45.98; H, 4.385.

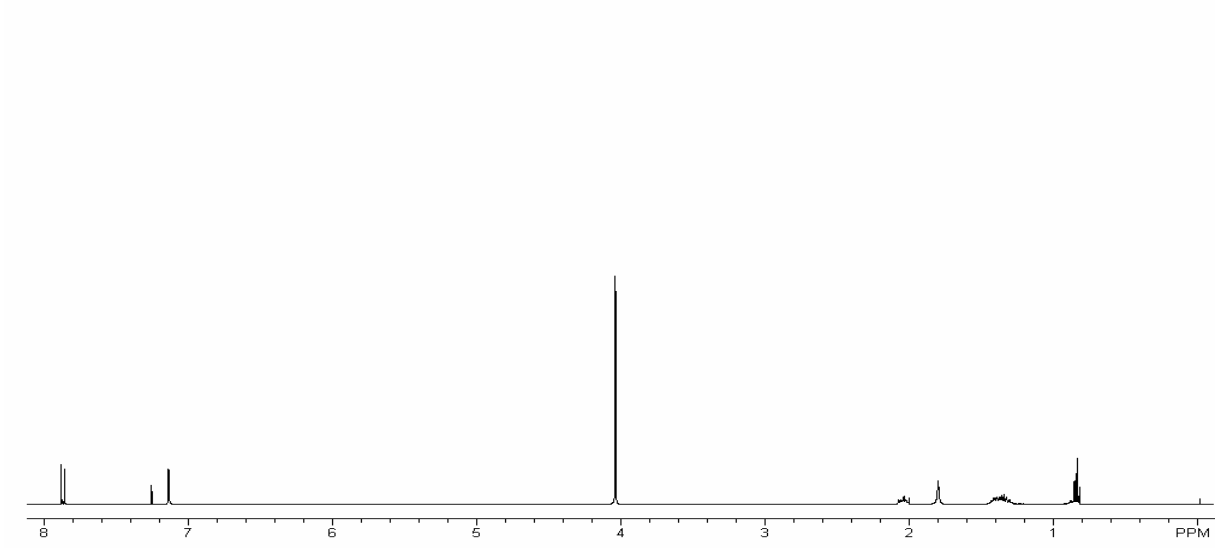


Figure 1. ^{1}H NMR of 2,7-Dibromo-3,6-dimethoxyl-9-butyl-9-phosphafluorene oxide in $CDCl_3$

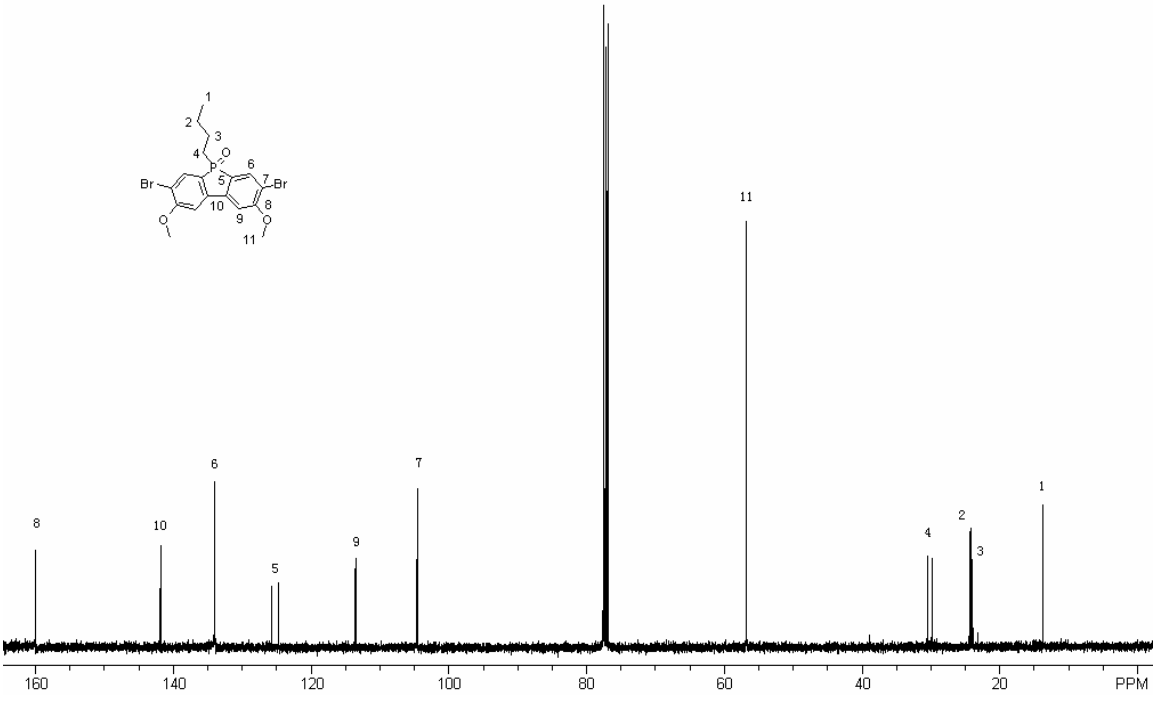


Figure 2. ^{13}C NMR of 2,7-Dibromo-3,6-dimethoxyl-9-butyl-9-phosphafluorene oxide in $CDCl_3$.

Poly[(9,9-dioctylfluorene)-co-(3,6-dimethoxyl-9-phenyl-9-phosphafluorene)]

(PFO-PhPF10)

Into a 20 mL flask were added 19.1 mg (0.04 mmol) 2,7-Dibromo-3,6-dimethoxyl-9-phenyl-9-phosphafluorene, 87.8 mg (0.16 mmol) 9,9-dioctylfluorene-2,7-dibromide, and 117 mg (0.21 mmol) 9,9-dioctylfluorene-2,7-bis(trimethylene boronate), 2 mg tetrakis(triphenylphosphine) palladium, and one drop of the phase transfer catalyst of Aliquat 336 in 10 mL anhydrous toluene. Subsequently, 2 M aqueous sodium carbonate (4 mL) deaerated for 2 h was added into to the reaction solution. The mixture was stirred at 90 °C for 3 days, and then the polymerization was end-capped with excess amount of phenylboronic acid for 6 h, followed by bromobenzene for another 6 h. The reaction mixture was cooled to about 50 °C and added slowly to a vigorously stirred mixture of 400 mL methanol and 20 mL water. The polymer fibers were collected by filtration and reprecipitation from methanol. The recollected polymer was purified further by washing for 2 days in a Soxhlet apparatus with acetone to remove oligomers and catalyst residues. The final polymers were obtained after drying in vacuo at 40 °C, yielding 75%.

Poly[(9,9-dioctylfluorene)-co-(3,6-dimethoxyl-9-butyl-9-phosphafluorene oxide)]

(PFO-BuPFO10)

PFO-BuPFO10 was prepared in the same procedure as PFO-PhPF10.

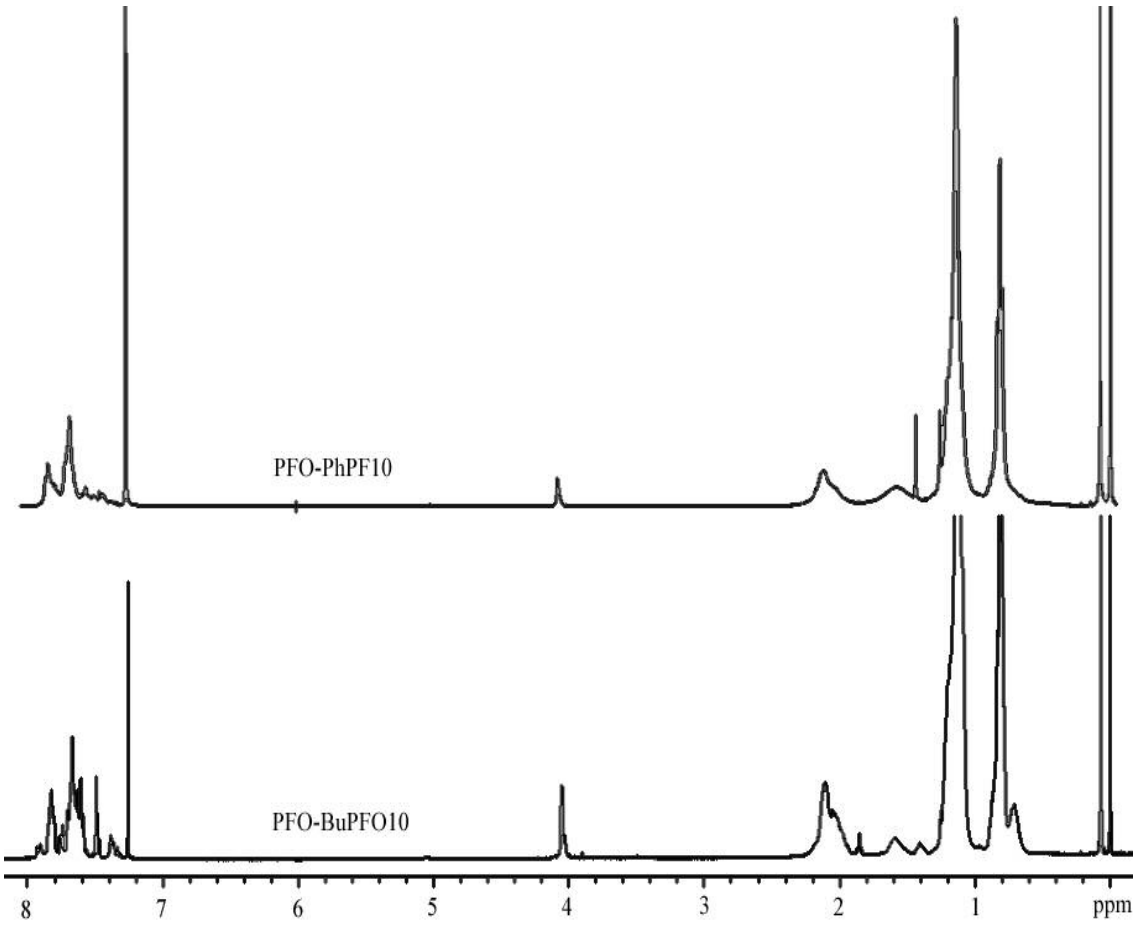


Figure 3. The ^{1}H NMR of PFO-PhPF10 and PFO-BuPFO10 in $CDCl_3$

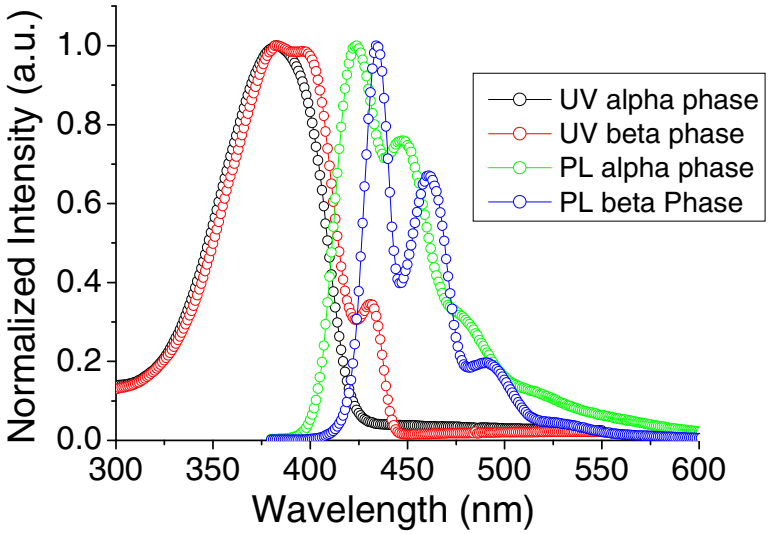


Figure 4. The α and β phase spectra of PFO in the solid film.

[1] M. Ranger, D. Rondeau, M. Leclerc, *Macromolecules* **1997***, 30*, 7686-7691.

[2] R.-F. Chen, Q.-L. Fan, C. Zheng, W. Huang, *Org. Lett.* **2006***, 8*, 203-205.