Supporting Information

Copolyfluorenes Containing Partially Hydrolyzed Phosphonate Pendant Groups: Synthesis, Characterization and Application as Electron Injection Layer for Enhanced Electroluminescence of PLEDs

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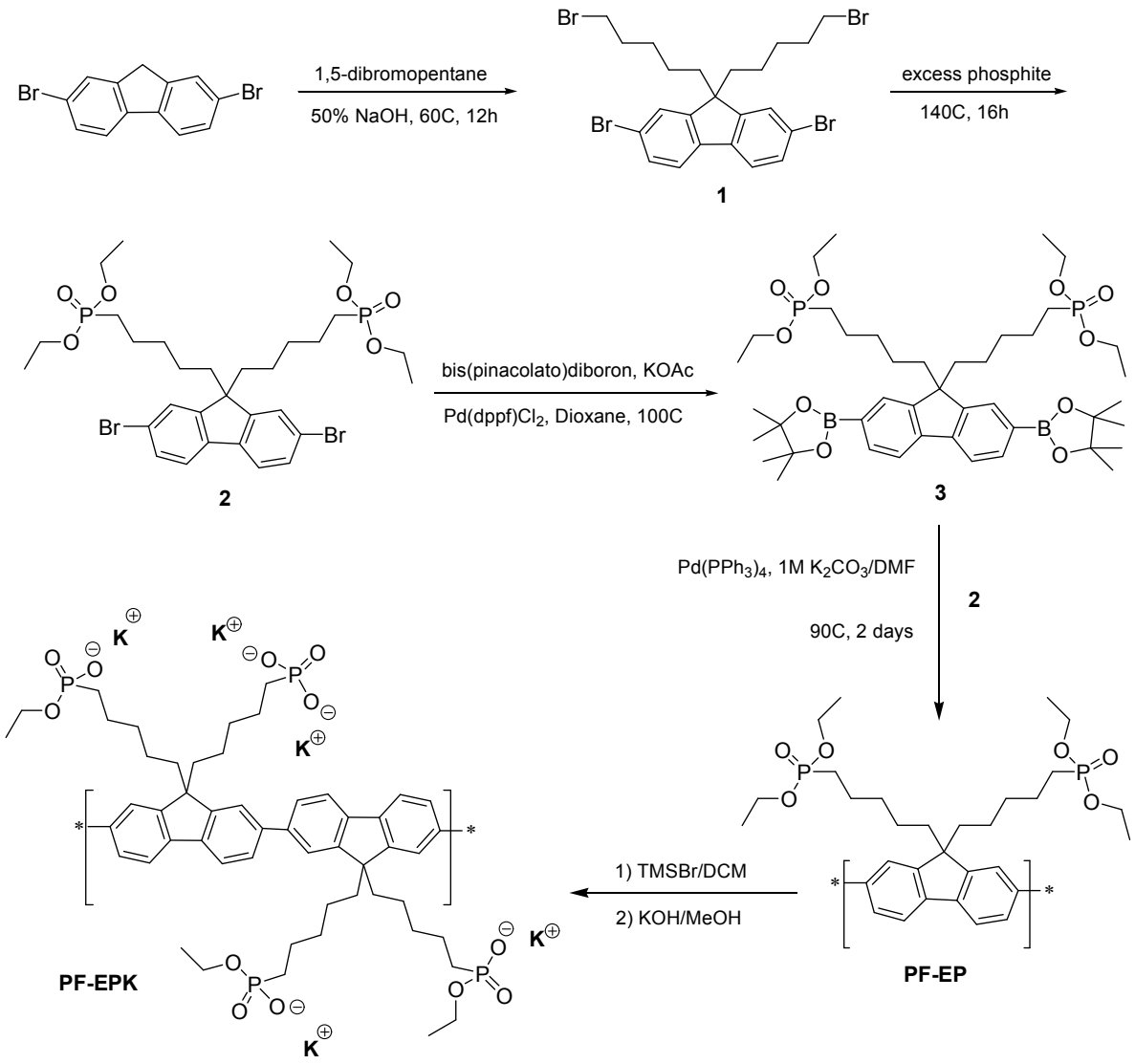
2,7-dibromo-9,9-bis(5'-bromopentyl) fluorene (1)

A two-phase mixture of 2,7-dibromofluorene (5.0 g, 15.4 mmol), 1,5-dibromopropane (14.2 g, 61.7 mmol), tetrabutylammonium bromide (0.5 g, 1.55 mmol), and 50 wt% sodium hydroxide aqueous solution was stirred at 60 °C overnight under nitrogen. After diluting the reaction mixture with water, the organic layer was extracted with water and dichloromethane. The separated organic layer was collected and dried over magnesium sulfate, and dichloromethane was evaporated to obtain crude solids. The solids were purified by column chromatography (dichloromethane and hexane as the eluent) and recrystallization to obtain white monomer **1** (yield: 44%). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm.): δ 7.52~7.54 (d, 2H, Ar-H), 7.46~7.48 (d, 2H, Ar-H), 7.44 (s, 2H, Ar-H), 3.22~3.24 (t, 4H, -C$\underline{H_2}$Br), 1.93~1.96 (m, 4H, -C$\underline{H_2}$-), 1.60~1.65 (m, 4H, -C$\underline{H_2}$-), 1.19~1.24 (m, 4H, -C$\underline{H_2}$-), 0.58~0.63 (m, 4H, -C$\underline{H_2}$-).Anal. Calcd. For $C_{13}H_8Br_2$: C, 44.40 %; H, 4.24 %. Found: C, 44.41 %; H, 4.21 %. Mp: 125-130 °C.



Scheme 1. Synthesis of **PF-EP** and **PF-EPK**.

2,7-dibromo-9,9-bis(5'-diethoxylphosphorylpentyl)-fluorene (2)

2,7-dibromo-9,9-bis(5'-bromopentyl) fluorene (**1**) (5.0 g, 8.04 mmol) was dissolved in excess amount of triethyl phosphite and heated to 140 °C for 16 h. Then the excess triethyl phosphite was removed by reduced pressure, and monomer **2** was obtained as colorless oil after purification with chromatography (acetone and dichloromethane as the eluent) (yield: 87%). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm.): δ 7.52~7.53 (d, 2H, Ar-H), 7.46~7.47 (d, 2H, Ar-H), 7.42 (s, 2H, Ar-H), 4.01~4.05 (m,

8H, -O-C$\underline{H_2}$-), 1.91~1.93 (m, 4H, -C$\underline{H_2}$-), 1.51~1.56 (m, 4H, -C$\underline{H_2}$-), 1.33~1.37 (m, 4H, -C$\underline{H_2}$-), 1.26~1.29 (t, 12H, -C$\underline{H_3}$), 1.13~1.18 (m, 4H, -C$\underline{H_2}$-), 0.57~0.59 (m, 4H, -C$\underline{H_2}$-). Anal. Calcd. For $C_{31}H_{46}Br_2O_6P_2$: C, 50.56 %; H, 6.30 %. Found: C, 48.73 %; H, 6.47 %.

2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(5'-diethoxyl-phosphorylpentyl)fluorene (3)

A solution of 2,7-dibromo-9,9-bis(5'-diethoxylphosphorylpentyl)-fluorene (**2**) (2.0 g, 2.72 mmol), bis(pinacolato)diboron (2.1 g, 8.16 mmol), and potassium acetate (1.81 g, 18.44 mmol) in dry 1,4-dioxane (10 ml) with little amount of $Pd(dppf)Cl_2$ was heated to 80 ºC overnight. The 1,4-dioxane was removed under reduced pressure and the solids were dissolved in dichloromethane, followed by extracting with water . The separated organic layer was collected and dried over magnesium sulfate, and dichloromethane was evaporated to obtain crude residue. The residue was purified by column chromatography (acetone and hexane as the eluent) and recrystallization to give monomer **3** as white solid (yield: 75%). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm.): δ 7.78~7.79 (d, 2H, Ar-H), 7.69~7.70 (d, 4H, Ar-H), 3.95~4.00 (m, 8H, -O-C$\underline{H_2}$-), 1.96~1.99 (m, 4H, -C$\underline{H_2}$-), 1.45~1.48 (m, 4H, -C$\underline{H_2}$-), 1.37 (s, 24H, -C$\underline{H_3}$), 1.24~1.29 (m, 4H, -C$\underline{H_2}$-), 1.01~1.11 (t, 12H, -C$\underline{H_3}$), 0.49~0.54 (m, 4H, -C$\underline{H_2}$-).Anal. Calcd. For $C_{43}H_{70}B_2O_{10}P_2$: C, 62.18 %; H, 8.49 %. Found: C, 61.10 %; H, 8.52 %. Mp: 132 °C