**Supporting Information**

**Modification of pyridine-based conjugated polymer films via Lewis acid: halochromism, characterization and macroscopic gradation patterning**

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**Experimental**

**Materials**

Dry solvents, 37% HCl solution (Wako) and tetrafluoroborate-diethylether complex (BF₃-OEt₂) (Wako) were used as received. 2,5-dibromopyridine, 9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, tetrakis(triphenylphosphine) palladium, (Pd(PPh₃)₄), were used as received. 2,5-Bis(5-bromothiophen-2-yl)pyridine was synthesized according to the previous work. S1

**Synthesis of PP by Suzuki-Miyaura Coupling Polymerization**

2,5-Dibromopyridine (190 mg, 0.80 mmol), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (446 mg, 0.80 mmol), Pd(PPh₃)₄ (24 mg, 0.02 mmol), tetrabutylammonium bromide (3 mg) were dissolved in 8 ml of dry toluene under argon. To the solution were added K₂CO₃ (aq) (2.0 M, 4 ml). After stirred for 48 h at 100 °C, the reaction mixture was reprecipitated into a large amount of methanol. PP was collected by filtration, dried under vacuum, and obtained as a pale-yellow powder (460 mg). ¹HNMR (300 MHz, CDCl₃): δ 9.1 (Ar-H, s), 8.1-7.5 (Ar-H, br), 2.11
(CH₂(CH₂)₆CH₃, br), 1.25-0.77 (CH₂(CH₂)₆CH₃, br).¹³CNMR (75.45 MHz, CDCl₃): δ 152.2, 148.2, 138.1, 136.7, 135.0, 129.2, 129.0, 128.9, 128.7, 127.7, 127.6, 125.4, 124.5, 120.7, 120.6, 120.4, 117.3, 55.6, 40.5, 31.8, 30.1, 29.3, 23.9, 22.7, 14.2. GPC (polystyrene standard): Mₙ = 17,500, Mₘ = 38,800, Mₘ/Mₙ = 2.22.

**Synthesis of PTP by Suzuki-Miyaura Coupling Polymerization**

2,5-Bis(5-bromothiophen-2-yl)pyridine (20 mg, 0.05mmol), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (29 mg, 0.05mmol), Pd(PPh₃)₄ (3 mg, 0.0025mmol), tetrabutylammonium bromide (3 mg) were dissolved in 1 ml of dry toluene under argon. To the solution were added K₂CO₃ (aq) (2.0 M, 0.5 ml). After stirred for 72 h at 100 °C, the reaction mixture was reprecipitated into a large amount of methanol. PTP was collected by filtration, dried under vacuum, and obtained as a pale-orange powder (31 mg). ¹HNMR (300 MHz, CDCl₃): δ 8.9 (Ar-H, s), 7.9-7.2 (Ar-H, br), 2.05 (CH₂(CH₂)₆CH₃, br), 1.25-0.77 (CH₂(CH₂)₆CH₃, br). ¹³CNMR (75.45 MHz, CDCl₃): δ 152.4, 140.9, 129.2, 129.0, 128.9, 128.7, 127.7, 127.6, 125.4, 124.5, 120.7, 120.6, 120.4, 119.1, 55.6, 40.5, 31.8, 30.1, 29.3, 23.9, 22.7, 14.2. GPC (polystyrene standard): Mₙ = 5,200, Mₘ = 8,200, Mₘ/Mₙ = 1.58.

**Measurement**

Liquid-state ¹H NMR spectra were recorded on a JEOL EX-300 spectrometer. High-resolution solid-state ¹³C nuclear magnetic resonance spectra were measured using a Varian NMR systems 400WB spectrometer operating at 100.57MHz for ¹³C and 399.94 MHz for ¹H, and obtained by the combined use of cross polarization (CP) and magic-angle spinning (MAS) with ¹H high-power dipolar decoupling of 60 kHz under the MAS of 5 kHz. The utilized CP contact time was 2 ms. ¹⁹F MAS NMR spectra were measured using the same spectrometer operating at 376.25 MHz for ¹⁹F, and the 45 degree pulse of 7.5 μs was used under the MAS of 23 kHz. To obtain the ¹⁹F spin-lattice relaxation time (T₁ F), the conventional inversion-recovery method was employed with 90 degree pulse of 15 μs and 180 degree pulse of 33 μs. ¹³C chemical shifts were measured relative to TMS (tetramethylsilane) using the methine carbon signal at 29.47 ppm for solid adamantane as an external standard. ¹⁹F chemical shifts were relative to CFCI₃ referenced externally to the CF₂ signal of Teflon at -122 ppm. ¹²UV-vis absorption spectra were obtained on a Shimadzu UV-1800 spectrophotometer.
Photoluminescence (PL) spectra were obtained on a Shimadzu RF-5300PC spectrophotometer. GPC analyses were performed by a Shimadzu Prominence GPC system (Shim-pack GPC 803C column), using chloroform as the eluent after calibration with polystyrene standards.

Fig. S1. Solid-state $^{13}$C CPMAS NMR spectra of PP films. Symbol * represents the artificially appeared signal on MAS experiments, called as a spinning side band (SSB) of the intrinsic aromatic carbon signals observed from 110 to 160 ppm. Assignments are also depicted on figure.
Fig. S2. Plots of the normalized $^{19}$F peaks at -147 (●) and -152 ppm (○) for the inversion-recovery method to obtain $T_1^F$ value. The solid lines are the least-square fit to the conventional equation, $M(t) = 1 - p \cdot \exp (-t/T_1^F)$: $M(t)$ is normalized magnetization. The value of parameter $p$ ideally equals 2.

References
