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 (BF_3-OEt_2) (Wako) were used as received. 2,5-dibromopyridine, 9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester,tetrakis(triphenylphospine) palladium, ($Pd(PPh_3)_4$), 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),$Pd(PPh_3)_4$ (24 mg, 0.02mmol), tetrabutylammonium bromide (3 mg) were dissolved in 8 ml of dry toluene under argon. To the solution were added K_2CO_3 (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). ^{1}HNMR (300 MHz, $CDCl_3$): δ 9.1 (*Ar-H*, s),8.1-7.5 (*Ar-H*, br), 2.11

($CH_2(CH_2)_6CH_3$, br), 1.25-0.77 ($CH_2(CH_2)_6CH_3$, br).^{13}CNMR (75.45 MHz, $CDCl_3$): 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): M_n = 17,500, M_w = 38,800, M_w/M_n = 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),$Pd(PPh_3)_4$ (3 mg, 0.0025mmol), tetrabutylammonium bromide (3 mg) were dissolved in 1 ml of dry toluene under argon. To the solution were added K_2CO_3 (aq) (2.0 M, 0.5 ml). After stirred for 72 h at 100 ^{o}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). ^{1}HNMR (300 MHz, $CDCl_3$): δ 8.9 (*Ar-H*, s),7.9-7.2 (*Ar-H*, br), 2.05 ($CH_2(CH_2)_6CH_3$, br), 1.25-0.77 ($CH_2(CH_2)_6CH_3$, br). ^{13}CNMR (75.45 MHz, $CDCl_3$): 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): M_n = 5,200, M_w = 8,200, M_w/M_n = 1.58.

Measurement

Liquid-state ^{1}H NMR spectra were recorded on a JEOL EX-300 spectrometer. High-resolution solid-state ^{13}C nuclear magnetic resonance spectra were measured using a Varian NMR systems 400WB spectrometer operating at 100.57MHz for ^{13}C and 399.94 MHz for ^{1}H, and obtained by the combined use of cross polarization (CP) and magic-angle spinning (MAS) with ^{1}H high-power dipolar decoupling of 60 kHz under the MAS of 5 kHz. The utilized CP contact time was 2 ms.^{19}F MAS NMR spectra were measured using the same spectrometer operating at 376.25 MHz for ^{19}F, and the 45 degree pulse of 7.5 μs was used under the MAS of 23 kHz. To obtain the ^{19}F spin-lattice relaxation time (T_1^F), the conventional inversion-recovery method was employed with 90 degree pulse of 15 μs and 180 degree pulse of 33 μs.^{13}C chemical shifts were measured relative to TMS (tetramethylsilane) using the methine carbon signal at 29.47 ppm for solid adamantane as an external standard.^{19}F chemical shifts were relative to $CFCl_3$ referenced externally to the CF_2 signal of Teflon at -122 ppm.[S2] UV-vis absorption spectra were obtained on a Shimadzu UV-1800 spectrophotometer.

Photoluminescence (PL) spectra were obtained on a Shimadzu RF-5300PC spectrophotomerter. 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.

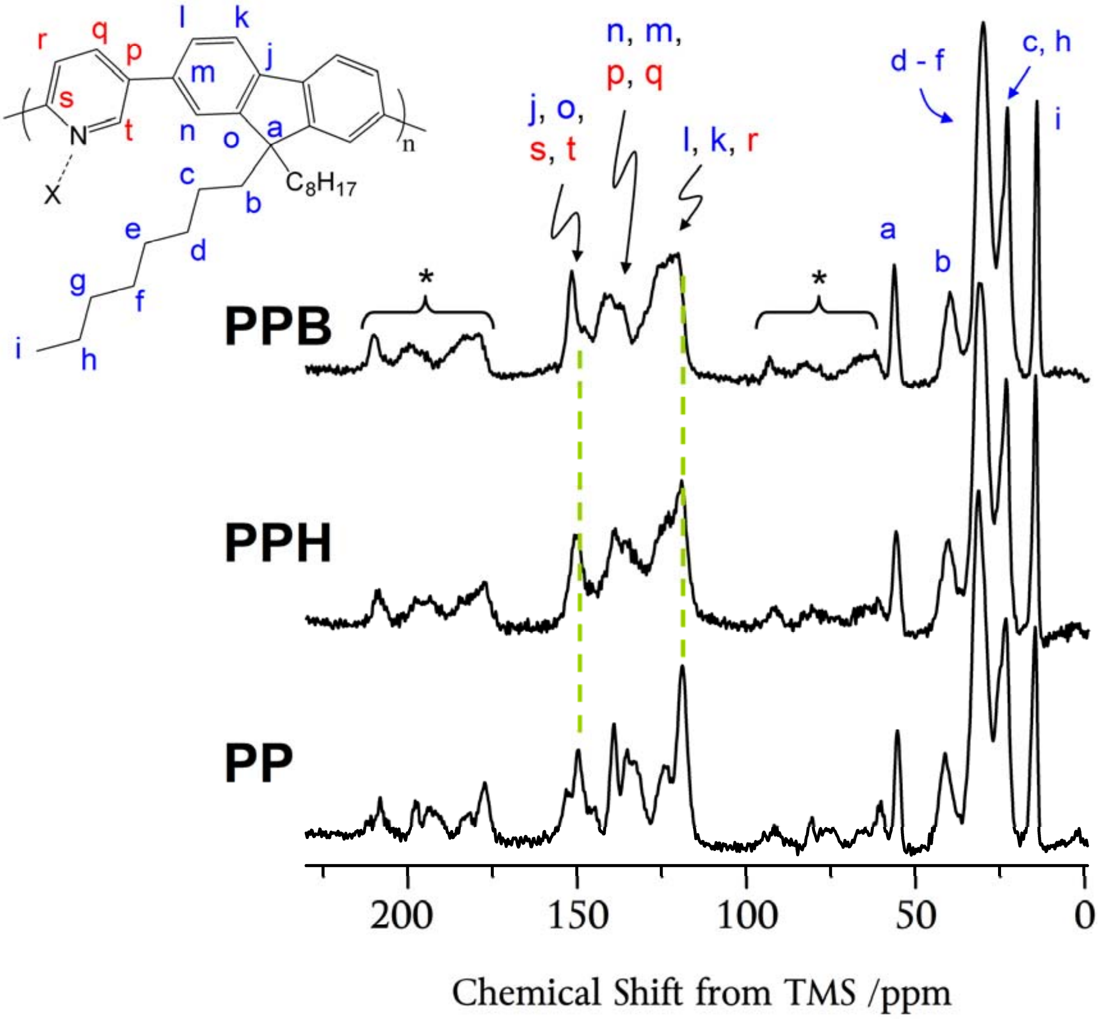

Fig. S1. Solid-state ^{13}C CPMAS NMR spectra of **PP** films.Symbol * represents the artificially appeared signal on MAS experiments, called as a spinning side band (SSB) of the intrinsic aromatic carbon signals observed from 110 to 160 ppm. Assignments are also depicted on figure.

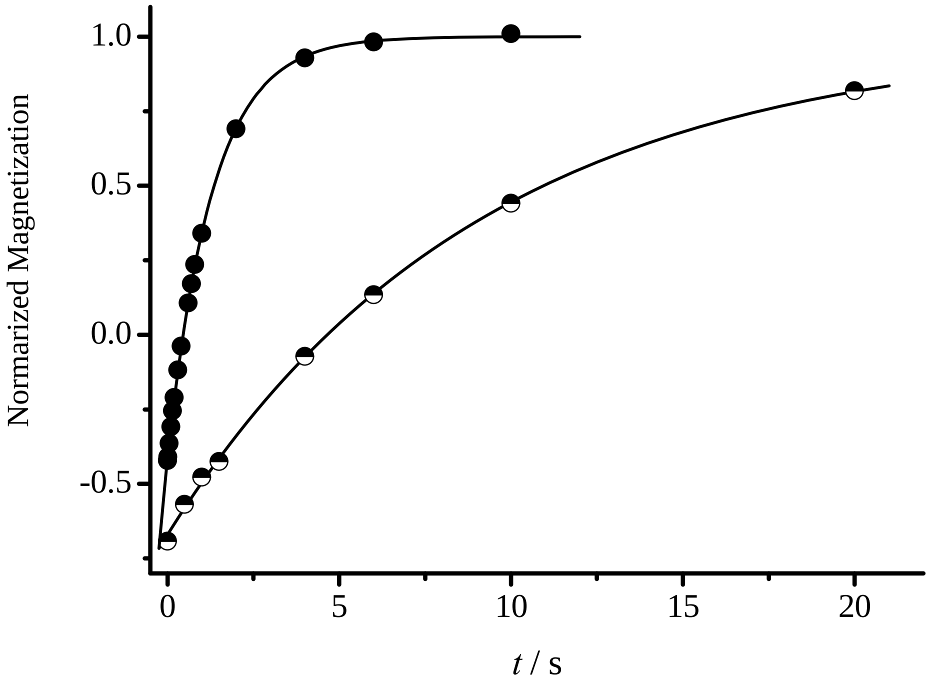

Fig. S2. Plots of the normalized ^{19}F peaks at -147 (●) and -152 ppm (◓) for the inversion-recovery method to obtain T_1^F value. The solid lines are the least-square fit to the conventional equation, $M(t) = 1 - p \cdot \exp(- t/T_1^F)$: $M(t)$ is normalized magnetization. The value of parameter p ideally equals 2.

References

S1) Y. K. Jung, J. Lee, S. K. Lee, H-J. Cho, H-K. Shim, *J. Polym. Sci: Part A: Polym. Chem.* 2006, **44**, 4611-4620.

S2) B. Fuchs, U. Scheler, *Macromolecules*, 2000, **33**, 120–124.