Supporting Information for

Synthesis of Novel Poly(tetramethyl-2,7-silpyrenylenesiloxane) and its Thermal and Optical Properties

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Experimental

Measurement

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400F spectrometer in deuterated chloroform ($CDCl_3$) or dimethylsulfoxide [$(CD_3)_2SO$] at ambient temperature. IR spectra were measured on a Perkin-Elmer Spectrum One FT-IR spectrometer. Melting point (T_m) was determined by differential scanning calorimetry (DSC) on a RIGAKU ThermoPlus DSC 8230 at a heating rate of 10 °C/min under a nitrogen flow rate of 10 mL/min. Thermogravimetry analysis (TGA) was performed on a RIGAKU ThermoPlus TG8110 at a heating rate of 10 °C/min under a nitrogen atmosphere. Number-averaged (M_n) and weight-averaged (M_w) molecular weights were estimated by size-exclusion chromatography (SEC) on a SHOWA DENKO Shodex GPC-101 system with polystyrene gel columns (a pair of Shodex GPC LF-804), eluted with THF using a calibration curve of polystyrene standards. Gas chromatography-mass spectroscopy (GC/MS) was carried out using a Shimadzu GCMS-QP2020A instrument. Absorption spectra were measured on a Shimadzu UV-2450 spectrophotometer. Emission spectra were measured on a Shimadzu RF-5000s spectrophotometer by use of the solution degassed by argon bubbling for 30 min. Fluorescence quantum yield of pyrenylene derivatives were measured using a HAMAMATSU PHOTONICS C9920-02 absolute PL quantum yield measurement system.[1]

Materials

2,7-Dibromopyrene (**1**) was prepared from pyrene (Aldrich) according to the literature.[2] *n*-Butyllithium in hexane solution (2.6 mol/L, KANTO KAGAKU), chlorodimethylsilane (ACROS Organics), 5% palladium on a charcoal (Wako Pure Chemical Industries, Ltd.) were commercially available and used as received. 1,1,3,3-Tetramethylguanidinium 2-ethylhexanoate was obtained from the equimolar mixture of 1,1,3,3-tetramethylguanidine and 2-ethylhexanoic acid (Tokyo Kasei Kogyo Co., Inc.). Chlorobenzene (KANTO KAGAKU) was used after distillation over calcium hydride. Tetrahydrofuran (THF, Wako Pure Chemical Industries, Ltd.) was used after distillation over sodium. The purity of all synthesized low molecular weight compounds was confirmed to be over 99% from GC analysis.

2,7-Bis(dimethylsilyl)pyrene (2)

Under a dry argon atmosphere, 2.6 mol/L *n*-butyllithium in hexane (9.62 mL, 25 mmol) was added dropwise to the mixture of 2,7-dibromopyrene (**1**, 1.80 g, 5 mmol) and dry THF (50 mL) for 15 min at –78 °C. After the resulting yellow-colored solution was stirred for 2 h, chlorodimethylsilane (1.19 g, 12.5 mmol) was added to this solution at room temperature. The reaction mixture was added to this solution at room temperature. The reaction mixture was stirred for 12h and poured into 100 mL of 0.2 mol/L HCl aqueous solution with stirring. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography eluted with hexane (R_f value: 0.58). The collected fraction was concentrated under reduced pressure. The residue was recrystallized from methanol to afford **2** as colorless crystals with the yield of 49.5 % (0.788 g, 2.47 mmol).

T_m: 136 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.33 (s, 4H, pyrenyl protons), 8.07 (s, 4H, pyrenyl protons), 4.75 [sept, J=3.75

Hz, 2H, –Si(CH$_3$)$_2$–*H*], 0.55 [d, *J*=3.75 Hz, 12H, –Si(C*H*$_3$)$_2$–]. ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 135.2 (pyrenyl carbon), 130.6 (pyrenyl carbon), 130.5 (pyrenyl carbon), 127.4 (pyrenyl carbon), 125.1 (pyrenyl carbon), –3.4 [–Si(*C*H$_3$)$_2$–]. IR (KBr, cm^{-1}): 2108 (Si–H). Mass (EI, *m/z*, intensity): 318 (M$^+$, 100%), 259 (M$^+$– [Si(CH$_3$)$_2$–H], 83%).

2,7-Bis(dimethylhydroxysilyl)pyrene (M1)

Under a dry argon atmosphere, **2** (1.80 g, 5.65 mmol) dissolved in dry THF (14 mL) was added dropwise to a mixture of dry THF (7 mL), H_2O (0.28 g, 15.75 mmol) and 5% Pd-C (0.014 g, 0.007 mmol) at room temperature. The mixture was stirred for 3 h at ambient temperature and filtered. The solvent was removed under reduced pressure. The residue was recrystallized from toluene to afford **M1** as yellow needles with the yield of 68.8 % (1.362 g, 3.89 mmol).

T_m: 211 °C. ^{1}H NMR [400 MHz, (CD$_3$)$_2$SO, ppm]: δ 8.45 (s, 4H, pyrenyl protons), 8.19 (s, 4H, pyrenyl protons), 6.20 (s, 2H, –OH), 0.45 [s, 12H, –Si(C*H*$_3$)$_2$–]. ^{13}C NMR [100 MHz, (CD$_3$)$_2$SO, ppm]: δ 138.9 (pyrenyl carbon), 130.2 (pyrenyl carbon), 129.8 (pyrenyl carbon), 127.7 (pyrenyl carbon), 124.4 (pyrenyl carbon), 1.17 [–Si(*C*H$_3$)$_2$–]. IR (KBr, cm^{-1}): 3245 (–OH). Mass (EI, *m/z*, intensity): 350 (M$^+$, 100%), 335(M$^+$ – [CH$_3$], 99%).

Poly(tetramethyl-2,7-silpyrenylenesiloxane) (P1)

Under a dry atmosphere, 1,1,3,3-tetramethylguanidinium 2-ethylhexoate (0.02 g) was added to **M1** (0.451 g, 1.25 mmol) dissolved in chlorobenzene (6.5 mL), and the reaction mixture was refluxed for 12 h with stirring. The soluble parts in THF were poured into acetone (250 mL) to generate the pale yellow precipitates. Yield: 28.3 % (0.118 g, 0.350 mmol) as pale yellow solid.

T_m: 286 °C. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 8.30 (s, 4H, pyrenyl protons), 7.83 (s, 4H, pyrenyl protons), 0.57 [s, 12H, –Si(C*H*$_3$)$_2$–]. ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 137.4 (pyrenyl carbon), 130.5 (pyrenyl carbon), 129.6 (pyrenyl carbon), 127.4 (pyrenyl carbon), 125.1 (pyrenyl carbon), 1.22 [–Si(*C*H$_3$)$_2$–]. IR (KBr, cm^{-1}): 1052 (Si–O). M_n: 43000, M_w: 1.38 (estimated by SEC in THF eluent using polystyrene standards).

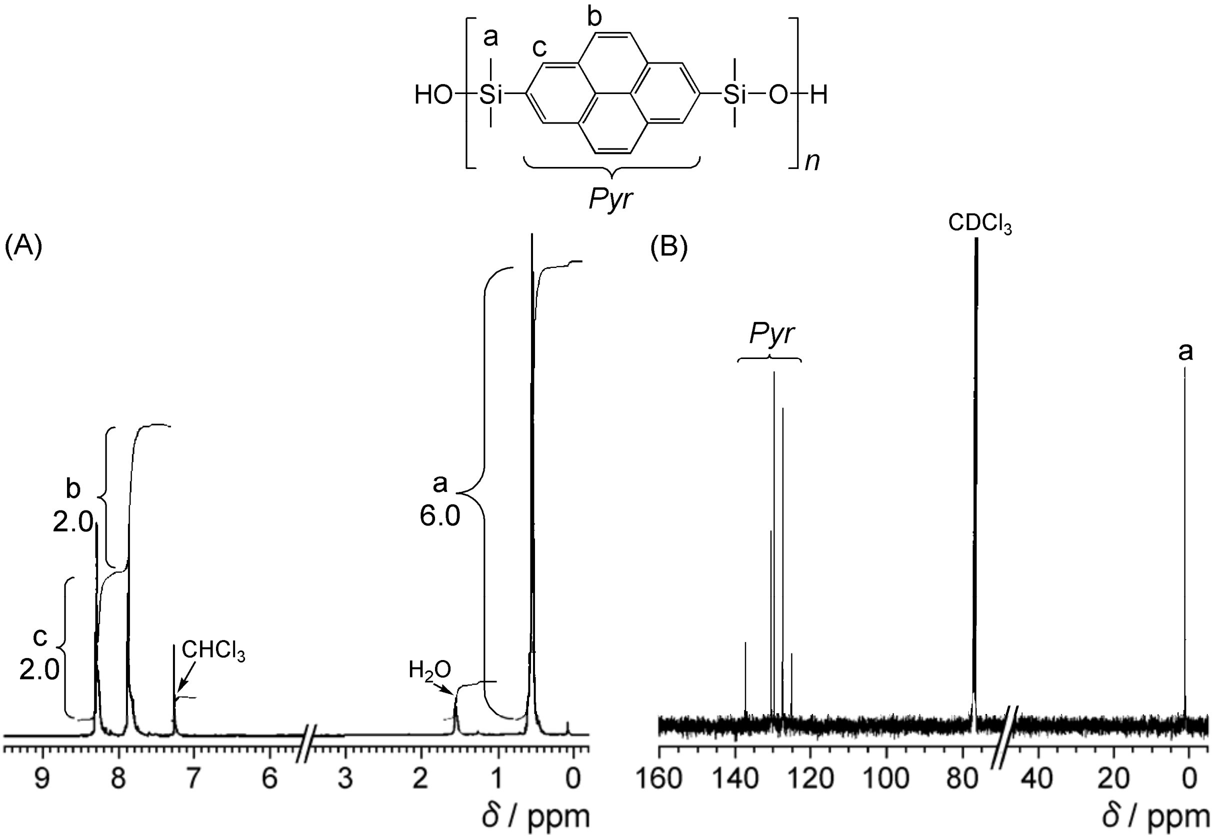

Figure S1. (A) ^{1}H NMR (in CDCl$_3$, 400 MHz, numerals at signal's side are the integral values of each signal) and (B) ^{13}C NMR (in CDCl$_3$, 100 MHz) spectra of **P1** at ambient temperature.

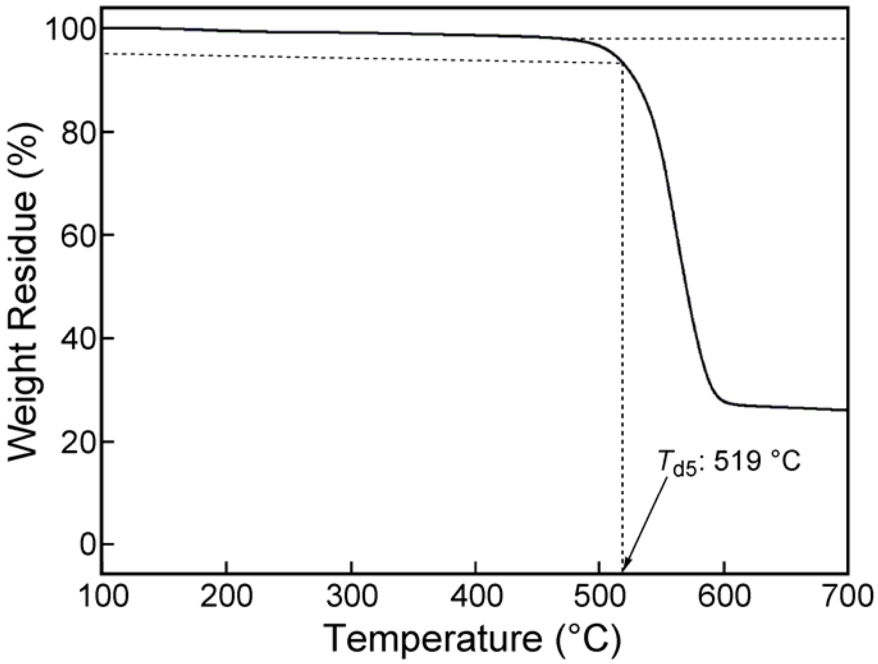

Figure S2. TG curve for **P1** at a heating rate of 10 °C/min under a nitrogen atmosphere.

References

1. Y. Kawamura, H. Sasabe, and C. Adachi, *Jpn. J. Appl. Phys.*, **43**, 7729 (2004).
2. a) H. Lee, R. G. Harvey, *J. Org. Chem*. **51**, 2847 (1986).
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Graphical Abstract

Novel poly(tetramethyl-2,7-silpyrenylenesiloxane) (**P1**) was obtained by polycondensation of a novel disilanol monomer, *i.e.*, 2,7-bis(dimethylhydroxysilyl)pyrene (**M1**). The temperature at 5% weight loss (T_{d5}) of **P1** was 519 °C, indicating the good thermostability of **P1**. The fluorescence quantum yields of **M1** and **P1** in chloroform solution were 0.49 and 0.39, respectively, and much larger than that of pyrene. The emission from **P1** was mainly resulted from the excimers, possibly owing to intra- and/or inter-molecular interactions between the pyrenylene moieties in **P1**.