Electronic Supporting Information for

Semi-Perfluoroalkyl Polyfluorene with Varying Fluorine Content: Synthesis and Photophysical Properties

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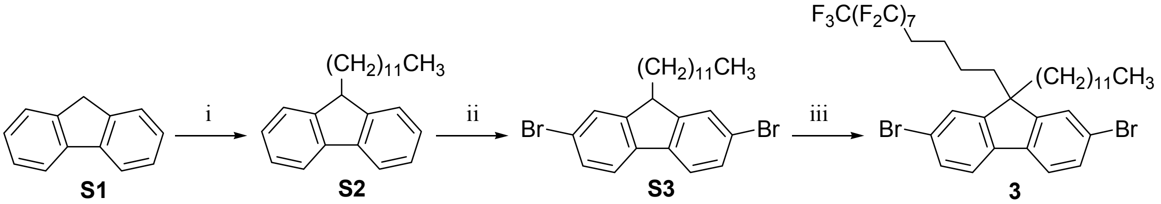
General experimental details

Instrumentation

^{1}H NMR spectra were recorded on Bruker-Biospin Advance (800 MHz) or Varian Unity (500 MHz) instruments at 25 °C, using $CDCl_3$. The chemical shift data for each signal are given as δ in units of parts per million (ppm) relative to tetramethylsilane (TMS) where δ(TMS) = 0.00 ppm. The multiplicity of each signal is indicated by: s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet) and br m (broad multiplet). ^{13}C NMR spectra were recorded on a Varian Unity 500 (125 MHz) or Bruker-Biospin Avance (200 MHz) instrument using the central resonance of the triplet of $CDCl_3$ at δ 77.0 ppm as an internal reference. For fluorinated compounds, where the spectrum is noted as 'partial', the carbons substituted with one or more fluorines were not visible. Microanalyses were carried out by Chemical & Analytical Services Pty. Ltd. (Australia). Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. UV-Vis absorption spectra were recorded on a Varian Cary Bio 8G spectrometer. Solid state spectra were measured on thin films prepared by spin-coating. Photoluminescence emission spectra were measured at 25 °C using a Varian Cary Eclipse Fluorimeter. Photo Electron Spectroscopy in Air (PESA) measurements were recorded using a Riken Keiki AC-2 with a power number of 0.5. Solid state spectra were measured on thin films prepared by spin-coating. Mass spectra were recorded at CSIRO (CMSE, Clayton) or at the Bio21 Institute, The University of Melbourne or at the EPSRC National Mass Spectrometry Service Centre, Swansea. Low resolution spectra were recorded on a Waters Micromass Quattro II instrument (EI, ESI and CI). Thermo gravimetric analysis (TGA) was performed on a TA Instruments Q500 at a heating rate of 10 °C min^{-1} under N_2. The thermal transition behaviour of polymers was measured on a Perkin-Elmer differential scanning calorimeter. Each measurement was carried out with heating at 10 °C/min up to 300 °C with an isothermal period of 5 minutes (300 °C), followed by cooling at 10 °C/min to 25 °C, with a second isotherm of 5 minutes (25 °C). Size exclusion chromatography was performed on a Waters GPC system (Waters 486 UV detector) by eluting THF (1 cm^3 min^{-1}) at 40 °C, or by Asahi Glass Co. Ltd. (Japan) using 1,1-dichloro-2,2,3,3,3-pentafluoropropane as an eluant according to a published procedure.[1]

Materials

Tetrahydrofuran (THF) and diethyl ether were dried by passage through a packed column of activated neutral alumina under a N_2 atmosphere, and toluene by passage through a column with additional R3-11 copper-based catalyst (BASF Australia).[2] Light petroleum refers to the fraction of boiling point range 40–60 °C. Fluorene monomers **1**, **2**, **4** and **5** and polymers **P1** and **P5** have been described in the literature.[3] The synthesis of precursors **S2** and **S3** and monomer **3** are described below (Scheme S1). All other precursors and reagents were purchased from commercial suppliers and used without further purification.



Scheme S1. Synthesis of semi-perfluoroalkyl fluorene monomer **3**. Reagents and conditions: (i) dodecanol, KOH, 140 °C, 16 h,45%; (ii) iodine, bromine, CHCl3, 0 °C, 1 h, 25 °C, 16 h, 78%; (iii) 2.10, TBAB, 50% NaOH, toluene, 80 °C, 16 h, 28%.

Monomer synthesis

9-Dodecyl-9*H*-fluorene **S2**

9*H*-Fluorene **S1** (3.00 g, 18.0 mmol) was dissolved in dodecanol (16.80 g, 90.2 mmol) by heating gently whilst being stirred. Crushed KOH pellets (0.50 g, 9.0 mmol) were added and the reaction heated to 190 °C whilst being stirred in air for 16 h. The reaction was allowed to cool to 70 °C before being put under high vacuum for 15 min to eliminate water. The crude material (2.69 g, 45%) was obtained by column chromatography (light petroleum) and used in the next step without further purification, R_f (light petroleum) 0.3. δ_H (500 MHz, $CDCl_3$) 0.89 (t, *J* 7, 3H, CH_3), 1.26 (m, 20H, 10 × CH_2), 2.00 (m, 2H, CH_2), 3.98 (t, *J* 6, 1H, C*H*), 7.31 (dt, *J* 1 and 7, 2H, Ar*H*), 7.37 (m, Ar*H*), 7.52 (ddd, *J* 1, 2 and 7, 2H, Ar*H*), 7.76 (m, 2H, Ar*H*).

2,7-Dibromo-9-dodecyl-9*H*-fluorene **S3**

To a solution of **S2** (2.60 g, 7.70 mmol) in $CHCl_3$ (15 cm^3) was added I_2 (0.30 g, 1.16 mmol) in the dark. The reaction was cooled to 0 °C and Br_2 (1 cm^3, 9.40 mmol) was added via syringe. The reaction was allowed to warm to 25 °C whilst being stirred in the dark for 16 h. The reaction was quenched with dilute NaOH solution (100 cm^3) and poured into water. The aqueous phase was extracted with CH_2Cl_2 and the organic fractions were washed with sat. $NaHCO_3$ solution, water and brine. The organic fractions were dried ($MgSO_4$) and concentrated under reduced pressure. The crude material was recrystallised from ethanol to give the title compound **S3** as colourless crystals (2.98 g, 78%), mp 86-88 °C. ν_{max} (neat solid)/cm^{-1} 2918, 2850, 1739, 1599, 1569, 1451, 1417, 821, 812. δ_H (500 MHz) 0.88 (t, *J* 7, 3H, CH_3), 1.08–1.18 (m, 2H, CH_2), 1.18–1.34 (m, 18H, 9 × CH_2), 1.96 (m, 2H, CH_2), 3.94 (t, *J* 7, 1H, C*H*), 7.52 (dd, *J* 8 and 37, 4H, Ar*H*), 7.62 (s, 2H, Ar*H*). δ_C (125 MHz) 14.1, 22.7, 25.4, 29.3, 29.55, 29.6, 29.65, 29.8, 31.9, 32.7, 47.5, 121.11, 121.13, 127.6, 130.2, 139.1, 149.3. *m/z* (ESI) 494.1 (50%, $C_{25}H_{32}{}^{81}Br_2$), 492.1 (100%, $C_{25}H_{32}{}^{79}Br^{81}Br$), 490.1 [49%, $C_{25}H_{32}{}^{79}Br_2$ (M^+)], 322.9 (31%), 243.0 (37%). Anal. Calc. for $C_{25}H_{32}Br_2$: C 61.0, H 6.55. Found: C 60.95, H 6.55%.

2,7-Dibromo-9-dodecyl-9-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorododecyl)fluorene **3**

To a solution of **S3** (2.56 g, 5.20 mmol) and 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorododecyl iodide[4] (4.70 g, 7.80 mmol) dissolved in toluene (10 cm^3) was added 50% NaOH solution (10 cm^3) and Bu_4NBr (0.83 g, 2.6 mmol). The reaction was heated to 80 °C and allowed to stir for 16 h. The reaction was poured into water and extracted with Et_2O. The organic fractions were washed with 1 M HCl (2 × 100 cm^3), water and brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (light petroleum), and recrystallisation from a propan-2-ol and light petroleum mixture gave the title compound **3** as colourless crystals (1.41 g, 28%), R_f (light petroleum) 0.5. mp 61-63 °C. ν_{max} (neat solid)/cm^{-1} 2920, 2850, 1449, 1230, 1197, 1143, 1112. δ_H (500 MHz) 0.55-0.67 (m, 4H, 2 × CH_2), 0.87 (t, *J* 7, 3H, CH_3), 1.05-1.28 (m, 18H, 9 × CH_2), 1.38 (m, 2H, CH_2), 1.81 (m, 2H, CH_2), 1.93 (m, 2H, CH_2), 1.97 (m, 2H, CH_2), 7.46 (m, 4H, Ar*H*), 7.53 (d, *J* 8, 2H, Ar*H*). δ_C (125 MHz, partial) 14.1, 20.29, 20.3, 22.7, 23.3, 23.6, 29.2, 29.3, 29.5 (d, $J_{F,C}$ 4), 29.6, 29.8, 30.7, 31.9, 39.9, 40.2, 55.5, 121.2, 121.65, 126.1, 130.4, 139.1, 151.9. *m/z* (ESI) 968.0 (55%, $C_{37}H_{39}{}^{81}Br_2F_{17}$), 966.0 (100%, $C_{37}H_{39}{}^{79}Br^{81}Br$, F_{17}), 964.0 [53%, $C_{37}H_{39}{}^{79}Br_2F_{17}$, ($M^+$)], 717.9 (34%), 322.9 (47%). *m/z* (HRMS, EI) 964.1158 (964.1158 calc. for $C_{37}H_{39}Br_2F_{17}$). Anal. Calc. for $C_{37}H_{39}Br_2F_{17}$: C 46.0, H 4.1. Found: C 46.0, H 4.0%.

Photophysical Data

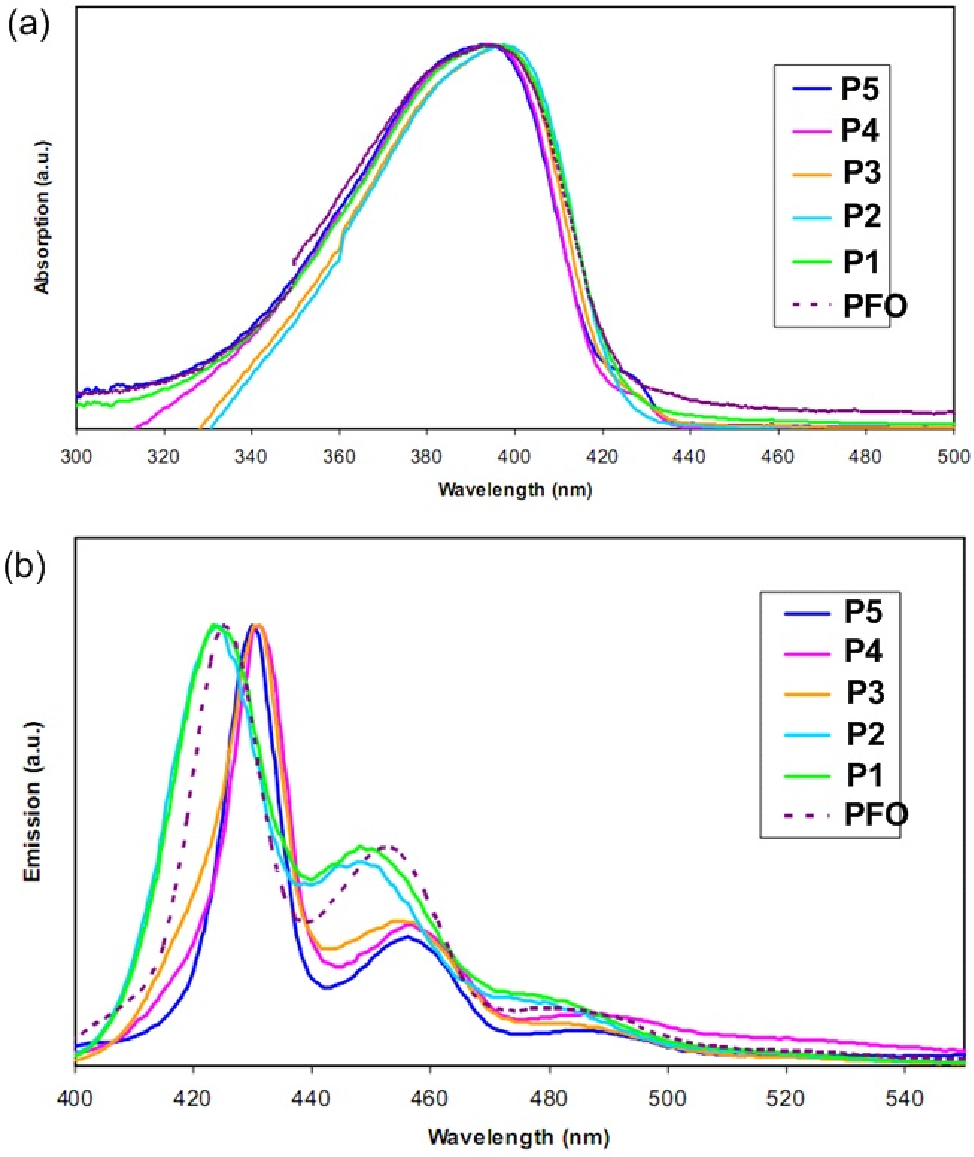


Figure S1. (a) Thin film UV-vis and (b) PL spectrum of polymers **P1** to **P5**.

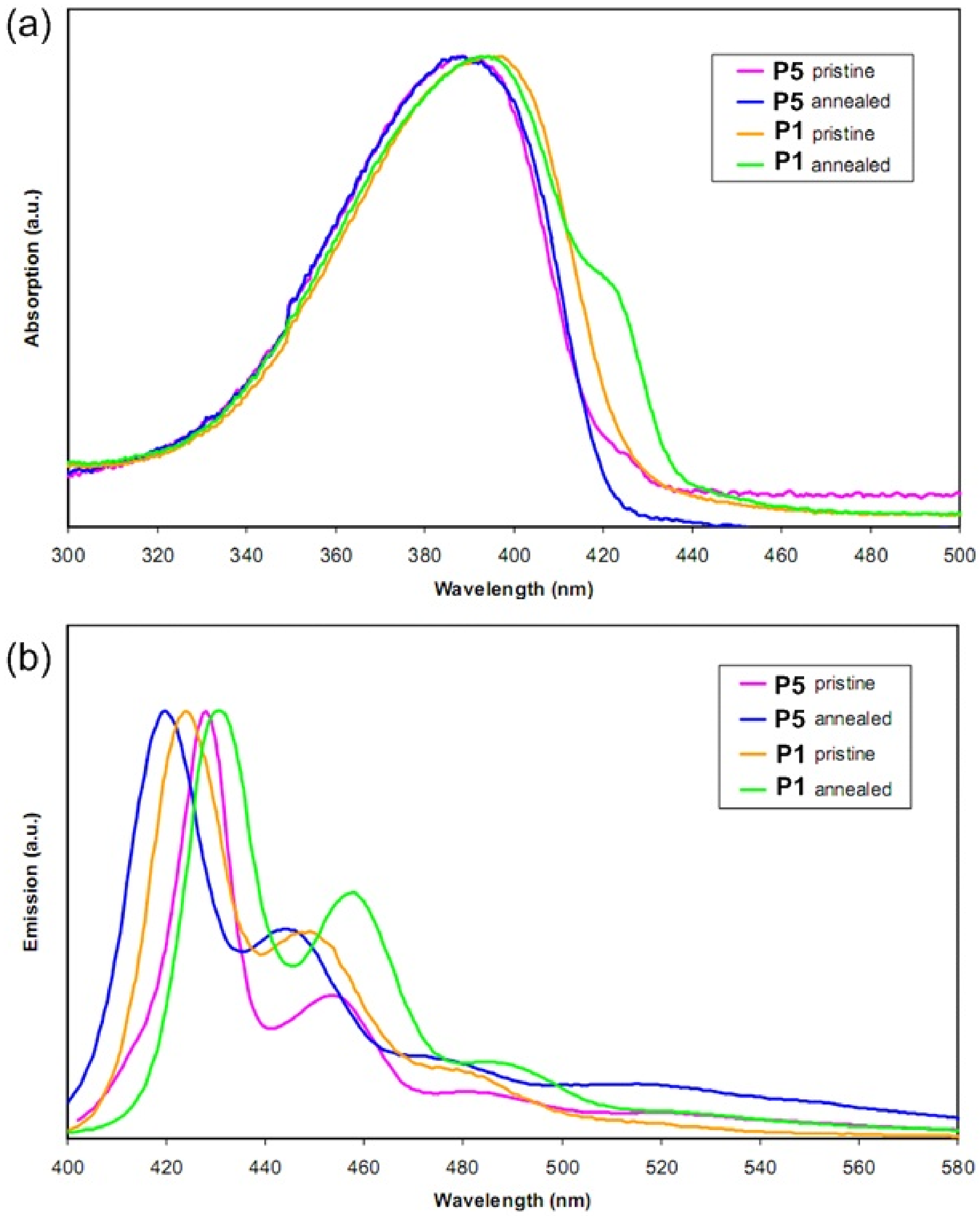


Figure S2. (a) Thin film UV-vis and (b) PL spectrum of polymers P1 and P5 as casted and after thermal annealing 120 °C 2 min in air.

References

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