

An alignable fluorene thienothiophene copolymer with deep-blue electroluminescent emission at 410 nm

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5 Electronic supplementary information:

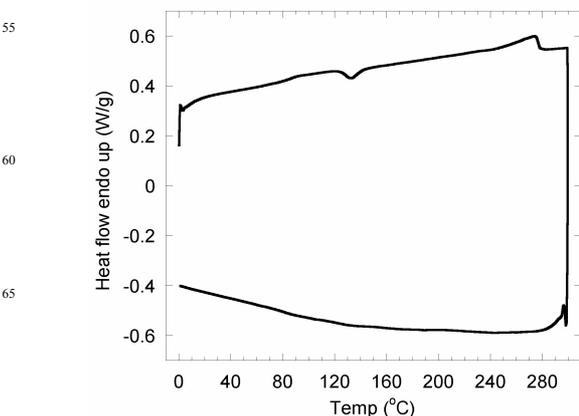
Materials and Measurements: ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-300 (300 MHz), using the residual solvent resonance of CDCl_3 as an internal reference and are given in ppm. Microanalyses were obtained with an elemental vario EL analyzer. Mass spectra were obtained either on an Agilent GCMS using a 6890 series GC with a 5973 MSD (EI). Molecular weight determinations were carried out in chlorobenzene solution at 60°C on an Agilent 1100 series HPLC using two Polymer Laboratories mixed B columns in series, and the system was calibrated against narrow weight PL polystyrene calibration standards. DSC measurements were performed on a TA Q100 under nitrogen. Reactions utilising microwave heating were performed on an Emrys Creator from Personal Chemistry Ltd. All starting materials and reagents were purchased from Aldrich Chemicals and Lancaster Chemicals. Anhydrous solvents were purchased from Romil Ltd and transferred using standard Schlenk line techniques. Column chromatography and TLC were performed on silica gel 60 (70-230 mesh, Merck) and silica gel F₂₅₄ plates (Merck) respectively.

2,5-Dibromo-3,4-dimethylthiophene: To a solution of 3,4-dimethylthieno[2,3-b]thiophene-2,5 dicarboxylic acid (28.0 g, 0.11 mol) in NMP (800 ml) and water (50 ml) was added NBS (44 g, 0.25 mol) portionwise over 30 min. The mixture for stirred for 16 h at RT and then poured into water (1 L). The resultant precipitate was filtered and dried under vacuum. Purification by flash chromatography over silica (eluent: petrol) afforded the product as white crystals (27.4 g, 77%). Mpt $137\text{--}139^\circ\text{C}$. MS (EI) (326, t, M+). ^1H NMR (CDCl_3 , 300 MHz, ppm) δ 2.40 (s, 6H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 143.0, 133.2, 130.4, 110.2, 14.2. Found C, 29.6; H, 2.1. Calc. for $\text{C}_8\text{H}_6\text{S}_2\text{Br}_2$ C, 29.5; H, 1.9.

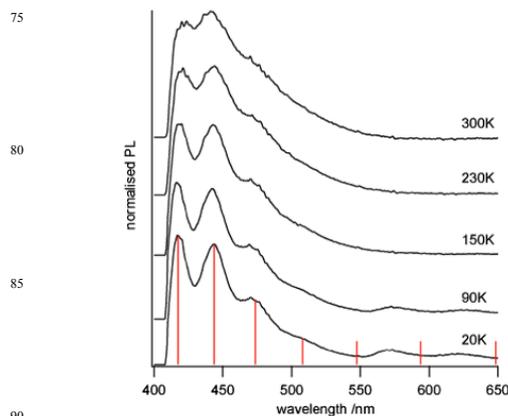
Poly(9,9-dioctylfluorene-co-3,4-dimethylthieno[2,3-b]thiophene): To a solution of 2,5-dibromo-3,4-dimethylthieno[2,3-b]thiophene (0.61 g, 1.88 mmol) and 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (1.05 g, 1.88 mmol) in anhydrous toluene (50 ml) under nitrogen was added tetrakis(triphenylphosphine)palladium (0) (100 mg, 0.086 mmol) followed by an aqueous solution of tetraethylammonium hydroxide (20 wt%, 10 ml). The resulting mixture was refluxed for 16 h, cooled and precipitated into methanol (200 ml) containing concentrated HCl (10 ml). The precipitate was filtered and washed (Soxhlet) with methanol, acetone and iso-hexane to afford a pale yellow powder (1.02 g, 97%).

GPC ($\text{C}_6\text{H}_5\text{Cl}$, 60°C) Mn 34,000, Mw 90,000 g/mol. ^1H NMR (CDCl_3 , 300 MHz, ppm) δ 7.80 (2H, d), 7.51 (4H, br s), 2.65 (6H, s), 2.04 (m, 4H), 1.3-1.1 (m, 24H), 0.83 (t, 6H). Found C, 79.6; H, 7.5. Calc. for $(\text{C}_{30}\text{H}_{32}\text{S}_2)_n$ C, 78.9; H, 7.1.

DSC:



70 *Photoluminescence measurements with temperature:*
PL spectra were recorded using an Oriel Instaspec CCD camera and an Oxford Instruments CCC1204 exchange gas cryostat.



LED fabrication and measurement: Indium tin oxide coated glass substrates were thoroughly cleaned in IPA and acetone before deposition of a 40 nm thick layer of PEDOT:PSS (Baytron P AI4083) under clean-room conditions. After transfer to a nitrogen glovebox (with active column-based water, solvent and oxygen removal) the substrates were heated to 200°C for 5 min to remove residual water before the F8TT layer was spin-coated from a toluene solution. The Ba/Al cathode layer was deposited by thermal evaporation under high vacuum ($< 4 \times 10^{-6}$ mbar). Current density-voltage-luminosity measurements were conducted using a luminance meter and Keithley source/measure units. EL spectra were recorded using an Oriel Instaspec CCD camera.

Aligned films: Orientation layers of rubbed polyimide were made from a two component polyimide precursor (Liquicoat PI ZLI 2650, Merck Chemicals) according to the standard procedure in the literature.²¹ A thin film of F8TT was deposited atop the alignment layer. Alignment of the film was achieved by annealing and subsequent quenching to room temperature within the confines of a nitrogen atmosphere glove box.

Polarized absorption and photoluminescent spectra were recorded within a Unicam UV/vis spectrophotometer equipped with a Glan-Thompson polarizer and a Fluoromax fluorescent spectrometer. Spectra were measured in parallel and perpendicular to the sample alignment direction.

Polarized Raman spectra were recorded with a Renishaw 2000 Raman spectrometer equipped with an Olympus BH-2 confocal microscope for light collection and a charge coupled device (CCD) detector. The sample was placed on a rotation stage and spectra were recorded with the sample oriented parallel and perpendicular to the electric field vector of the incident HeNe laser light. A polarization filter aligned parallel to this vector was placed in front of the detector. Due to the presence of residual fluorescence from the samples, a best-fit polynomial background correction was subtracted from each of the recorded spectra.

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