Luminescent poly(dendrimer)s for the detection of explosives

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Synthesis and Characterisation

Solvents were distilled before use. Freshly distilled dichloromethane and tetrahydrofuran were used for the electrochemical measurements. The dichloromethane was dried over calcium hydride before distillation and the tetrahydrofuran was refluxed over sodium prior to distillation. Light petroleum refers to the fraction with a boiling point range 40-60 °C. When solvent mixtures are used as the eluent, the proportions are given by volume. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV500 or Bruker AS500 spectrometers. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent peak. Coupling constants (J) are given in Hertz (Hz) and are quoted to the nearest 0.5 Hz. Peak multiplicities are described in the following way: doublet (d), doublet of doublets (dd), multiplet (m); peak identities are described as CpH = cyclopentyl H, VinH = vinyl H, EHH = 2-ethylhexyl H, PrH = *n*-propyl H, TPAH = triphenylamine H, G1 = biphenyl dendron H, and FlH = fluorenyl H, NbH = norbornenyl H, BPH = branching phenyl H, SPH = surface phenyl H.

Elemental analysis was carried out using a Carlo Erba NCHS Analyser Model NA 1500 instrument or Thermo Scientific Flash*Smart* CHNS/O Elemental Analyser. GPC measurements were carried out on a Waters GPC 1515 system equipped with Empower software. The instrument was connected to a refractive index (RI) and an UV-Vis detector. Two types of columns Styro-gel HT-6E and Styro-Gel HT-3 were used to analyse the polymer samples. The columns were kept at 40 °C with a flow rate of 1 mL/min and no flow marker was used during the analysis. Polystyrene standards were used to create the calibration curve. Polymer samples were prepared in tetrahydrofuran at a concentration of 1 mg/mL and filtered through a 0.45 micron PTFE filter. High resolution electrospray ionisation accurate mass measurements (ESI-MS) were recorded in positive mode on an Orbitrap Elite MS (ESI-Orbitrap) via a HESI source. Matrix Assisted Laser Desorption Ionization-Time of Flight mass spectrometry (MALDI-TOF MS) measurements were recorded using positive reflection mode on a Bruker Autoflex III MALDI-TOF/TOF MSI mass spectrometer using a *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2propenylidene]malononitrile (DCTB) matrix. External calibration was performed with an ABsciex 6-peptide mix. Absorption spectra were measured on a Varian Cary 5000 UV-vis-NIR spectrophotometer using double-distilled toluene as the solvent. Infrared absorption spectra were measured on a Perkin-Elmer Spectrum 100 FT-IR spectrometer as neat samples using an Attenuated Total Internal Reflection (ATR) interface. Differential scanning calorimetry (DSC) was performed on a PerkinElmer Pyris Diamond DSC. Thermal gravimetric analysis (TGA) was carried out on a Perkin-Elmer STA 6000 Simultaneous Thermal Analyser under nitrogen. Decomposition temperatures (T_d) are reported for a 5% decrease in sample mass corrected for the crucible. Melting points were measured in a glass capillary using a Büchi Melting Point B-545 apparatus and are uncorrected. Oxidation potentials [$E_{1/2(Ox)}$] were recorded with a BASi EpsilonEC using platinum working and reference electrodes and a 0.1 M $Ag/AgNO_3$ in acetonitrile reference electrode. Freshly distilled dichloromethane was used as the solvent, and the concentration of active species was approximately 1 mM. 0.1 M Tetra(*n*-butyl)ammonium tetrafluoroborate was used as the electrolyte, and the scan rate was 100 mV s^{-1}. The potentials are reported relative to the ferrocene/ferrocenium couple.

Spectroscopic Measurements

Samples of **M1-3** and **P1-3** were dissolved in double-distilled dichloromethane, double-distilled toluene, or chloroform (ACS *spectrophotometric grade*, ≥99.8%). Absorption spectra were measured on a Varian Cary 5000 UV-vis-NIR spectrophotometer. Photoluminescence spectra were recorded on a Horiba Jobin-Yvon Fluorolog-3 instrument with samples dissolved in double-distilled toluene. Solution PLQYs were measured relative to a reference quinine sulphate solution in 0.5 M sulphuric acid with a PLQY of 55%.[25] Solutions were optically dilute (absorbance ≈ 0.1 at excitation wavelength). The error of these measurements is estimated to be within ±10% of the reported value and the measured emission spectra were corrected for self-absorption.

Stern-Volmer Measurements

For the Stern-Volmer measurements the analytes were dissolved in solutions of the sensing materials, such that during the measurements only the analyte concentration varied, with the sensing material concentration remaining constant. For the steady-state measurements, 2.5 mL of material solution was placed in a 1 cm cuvette and the absorption and fluorescence spectra were measured. Multiple additions of a known volume of analyte solution were added to the cuvette with the absorbance and fluorescence spectra measured after each addition. The excitation wavelength selected for each sensor material and analyte combination was chosen to enable photo-excitation of the sensing material while minimising potential absorption by the analyte.

For the time-resolved Stern-Volmer measurements, 2.5 mL of material solution was placed in a 1 cm cuvette and excited with an LED with approximately 1 ns pulses at an excitation wavelength of 372 nm with a 1 MHz repetition rate. The fluorescence decays of the solutions were captured with a Horiba Jobin-Yvon Fluorolog 3 TCSPC system with an instrument response function (IRF) FWHM of approximately 1 ns. Multiple additions of a known volume of the analyte solution were added to the cuvette and the fluorescence decay was measured after each addition. All fits to the data were performed following convolution with the IRF.

*4-[9,9-Di-n-propyl-9H-fluoren-2-yl]-N-[4-(9,9-di-n-propyl-9H-fluoren-2-yl)phenyl]-N-[4-nitrophenyl]aniline (**4**)*

A mixture of 2-[9,9-di-*n*-propyl-9*H*-fluoren-2-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12.1 g, 32.2 mmol), 4-bromo-*N*-[4-bromophenyl]-*N*-[4-nitrophenyl]aniline[1] (4.08 g, 9.11 mmol), aqueous potassium carbonate (2 M, 25 mL) and toluene (75 mL) was degassed using three freeze-pump-thaw cycles, backfilling with argon, prior to the addition of *tetrakis*[triphenylphosphine]palladium(0) (0.150 g, 0.130 mmol). The reaction mixture was stirred at 100 °C overnight under argon, before being left to cool to room temperature. The reaction mixture was diluted with diethyl ether (200 mL) and washed with distilled water (200 mL). The organic phase was further washed with distilled water (2 × 100 mL), then brine (100 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated until approximately 100 mL of solution remained before being filtered through a celite plug using dichloromethane (1000 mL) as eluent. The solvent was removed from the filtrate to afford an orange solid (12.3 g), which was purified over silica using a dichloromethane:light petroleum mixture (1:1) as eluent to yield **4** as a yellow solid (6.52g, 91%). mp 270 °C; Found: C, 85.2; H, 6.9; N, 3.6. $C_{56}H_{54}N_2O_2$ requires: C, 85.5; H, 6.9; N, 3.6%; $\lambda_{max}(CH_2Cl_2)$/nm 279sh (log ε/dm^3 mol^{-1} cm^{-1} 4.47), 288sh (4.48), 317sh (4.63), 343 (4.70), 421 (4.37); ν_{max}/cm^{-1} 1583 (NO_2), 1296 (NO_2); δ_H(500 MHz; CD_2Cl_2) 0.63-0.73 (20H, m, PrH), 1.97-2.06 (8H, m, PrH), 7.09 and 8.09 (4H, AA'BB', TPAH), 7.31-7.37 (8H, m, TPAH and FlH), 7.38-7.41 (2H, m, FlH), 7.60-7.63 (4H, m, FlH), 7.71-7.76 (6H, m, TPAH and FlH), 7.78-7.81 (2H, m, FlH);

δ_C(125 MHz; CD_2Cl_2): 14.8, 17.8, 43.3, 55.9, 119.2, 120.3, 120.5, 121.8, 123.6, 125.9, 126.2, 127.2, 127.4, 127.7, 129.0, 139.4, 139.5, 141.0, 141.17, 141.19, 145.3, 151.6, 152.1, 153.9. Orbitrap-MS: Calc. for $C_{56}H_{54}N_2O_2$ $[M]^+$ = 786.4180 (100%), 787.4213 (61%), 789.4256 (18%), 789.4280 (4%). Found: 786.4195 (100%), 787.4231 (62%), 788.4264 (19%), 789.4296 (4%).

*(1S,2R)-N-[4-(Bis{4-[9,9-di-n-propyl-9H-fluoren-2-yl]phenyl}amino)phenyl]bicyclo[2.2.1]hept-5-ene-2-carboxamide (**M1**)*

Palladium on carbon (10% *w/w*, 0.141 g) was added to **4** (1.01 g, 1.27 mmol) dissolved in chloroform (60 mL) and ethanol (20 mL). The mixture was purged with hydrogen for 5 min before being left to stir in the dark overnight under hydrogen at room temperature. The reaction mixture was filtered through a celite plug, and the filtrate was collected and concentrated to give crude amine as a green solid (≈0.830 g), which was used without further purification. (1*S*,4*R*)-Bicyclo[2.2.1]hepta-2,5-diene-2-carboxylic acid (0.148 g, 1.07 mmol, 97% *exo*) was added to a solution of **5** (≈0.811 g, 1.07 mmol), *N*,*N*-dicyclohexylcarbodiimide (0.442 g, 2.14 mmol), 4-*N*,*N*-dimethylaminopyridine (0.263 g, 2.14 mmol) in distilled dichloromethane (15 mL), and then stirred for 16 h in the dark under argon at room temperature. The reaction mixture was diluted with dichloromethane (50 mL) and washed with water (3 × 50 mL) then brine (50 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and the solvent removed to afford a brown oil (1.21 g). The residue was purified by column chromatography over silica using ethyl acetate:light petroleum mixtures (0:100, 6:94, 20:80 as eluent. The product was collected as a purple solid (0.311 g), which was further purified by recrystallisation from an ethyl acetate:light petroleum mixture to yield **M1** as a white solid (0.248 g, 27%). mp 186 °C; Found: C, 87.6; H, 7.3; N, 3.2. $C_{64}H_{64}N_2O$ requires C, 87.6; H, 7.4; N 3.2%; $\lambda_{max}(CH_2Cl_2)$/nm 289 (log $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 4.57), 305sh (4.47), 358 (4.81); ν_{max}/cm^{-1} 3254 (NH) and 1650 (CO); δ_H(500 MHz; CD_2Cl_2) 0.62-0.74 (20H, m, PrH), 1.38-1.43 (2H, m, NbH), 1.75 (1H, d, J = 8.0, NbH), 1.94-2.07 (9H, m, PrH and NbH), 2.15-2.20 (1H, m, NbH), 2.96 (1H, brs, NbH), 3.05 (1H, brs, NbH), 6.16-6.22 (2H, m, NbH), 7.17 and 7.50 (4H, AA'BB', TPAH), 7.20 (4H, 1/2AA'BB', TPAH), 7.26 (1H, brs, NH), 7.28-7.36 (4H, m, FlH), 7.38 (2H, d, J = 7.5, FlH), 7.57-7.63 (8H, m, TPAH and FlH), 7.72 (2H, d, J = 7.0, FlH), 7.75 (2H, d, J = 8.0, FlH); δ_C(125 MHz; CD_2Cl_2) 14.9, 18.0, 31.2, 42.4, 43.4, 46.5, 46.9, 48.1, 56.0, 120.3, 120.6, 121.6, 121.7, 123.6, 124.4, 126.0, 126.2, 127.5, 127.7, 128.5, 136.2, 136.6, 139.2, 140.1, 140.7, 141.5, 147.6, 151.7, 152.1, 174.3; (MALDI-TOF, DCBT) Calc. for $C_{64}H_{64}N_2O$: 876.50 (100%), 877.50 (73%), 878.51 (26%), 879.51 (6%). Found: 876.32

(100%), 877.33 (87%), 878.39 (42%), 879.40 (12%); PL: λ_{max}(toluene)/nm 419, 440sh. PLQY (sol., toluene) 66%. CV: $E_{1/2}^{ox} = 0.2$ V *vs*. Fc/Fc$^+$.

*Poly[N-(4-{bis[4-(9,9-di-n-propyl-9H-fluoren-2-yl)phenyl]amino}phenyl)-2,4-divinylcyclopentane-1-carboxamide] (**P1**)*

M1 (1.47 g, 1.67 mmol) and freshly distilled anhydrous tetrahydrofuran (50 mL) were added to a Schlenk tube, then freeze-pump-thawed three times and backfilled with argon. The reaction vessel was covered with aluminium foil to protect the contents from light. Grubb's third generation catalyst (14.8 mg, 16.7 μmol) in freshly distilled anhydrous tetrahydrofuran (2 mL) was added rapidly to the stirred reaction mixture. The reaction mixture was stirred under argon at room temperature for 1.75 h before being quenched by the addition of ethyl vinyl ether (3 mL). The solution was concentrated until approximately 30 mL of solvent remained. The solution was added dropwise into methanol (100 mL). The resultant precipitate was collected at the filter, then washed with methanol (3 × 50 mL) and dried to yield **P1** a pale green solid (1.39 g, 95%). Found C, 86.9; H, 7.3; N, 3.1.5. $C_{64}H_{64}N_2O$ (repeating unit) requires C, 87.6; H, 7.4; N, 3.2%; ν_{max}/cm^{-1} 3345 (NH) and 1679 (CO); λ_{max}(toluene)/nm: 290sh, 354; δ_H(500 MHz, CD_2Cl_2): 0.40-0.75 (br, CpH and/or PrH), 0.95-1.30 (br, CpH), 1.40-1.75 (br, PrH), 1.80-2.10 (br, PrH), 2.10-2.50 (br, CpH), 2.50-2.86 (br, CpH), 2.86-3.30 (br, CpH), 5.00-5.70 (brm, VinH), 6.80-7.75 (brm, FlH, TPAH and NH); GPC: $\bar{M}_w = 1.9\times10^5$, $\bar{M}_n = 1.4\times10^5$, Đ = 1.4. $TGA_{(5\%)} = 430$ °C; PL: λ_{max}(toluene/nm) 437; PL: λ_{max}(40 nm neat film) 443; PLQY (sol., toluene) 59%; PLQY (50 nm neat film) 18%; CV: $E_{1/2}^{ox} = 0.3$ V *vs*. Fc/Fc$^+$.

*4,4,5,5-Tetramethyl-2-[9,9,9',9'-tetra-n-propyl-9H,9'H-(2,2'-bifluoren)-7-yl]-1,3,2-dioxaborolane (**2**)*

n-Butyllithium (2.5 M in hexanes, 5.28 mL, 13.2 mmol) was added to a solution of 7-bromo-9,9,9',9'-tetra-*n*-propyl-9*H*,9'*H*-2,2'-bifluorene[2] 3.70g, 6.57 mmol) in freshly distilled anhydrous tetrahydrofuran (40 mL) that had been cooled in a dry ice/acetone bath. The reaction was left to stir under argon for 45 min. 2-*iso*-Propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.02 mL, 9.90 mmol) was added, and the reaction was warmed to room temperature, before stirring for a further 1.5 h. Distilled water (150 mL) was added to the reaction mixture, which was then extracted with ethyl acetate (300 mL). The aqueous layer was further extracted with ethyl acetate (3 × 50 mL). The organic fractions were combined and washed with brine (100 mL), and then dried over anhydrous magnesium sulfate and filtered. The filtrate was collected and the solvent removed to yield a yellow, translucent solid. This solid was dissolved in dichloromethane (50 mL) and methanol (100 mL) was added, and then the solution was cooled to 0 °C and left for 2 h. Dichloromethane (~15 mL) was removed during which time a white precipitate formed. The white solid was collected at the filter and then washed with methanol (4 × 50 mL), dried at the filter, and then dried under high-vacuum to give **2** as a white, crystalline solid (2.65 g, 65%). mp 121 °C (from dichloromethane and methanol); Found: C, 85.0; H 8.6. $C_{44}H_{53}BO_2$ requires: C, 84.6; H, 8.6%; λ_{max}(CH_2Cl_2)/nm 237sh (log ε /$M^{-1}cm^{-1}$, 4.42), 265sh (3.83), 277sh (3.99), 289sh (4.19), 304sh (4.41), 336 (4.78); δ_H(500 MHz; CD_2Cl_2): 0.66-0.75 (20H, m, CH_2CH_3), 1.38 (12H, s, CH_3), 2.00-2.10 (8H, m, CH_2), 7.31-7.37 (2H, m, FlH), 7.39-7.41 (1H, m, FlH), 7.66-7.68 (4H, m, FlH), 7.74-7.83 (6H, m, FlH); δ_C(125 MHz, CD_2Cl_2): 14.8, 17.8, 25.3, 43.3, 56.0, 84.3, 119.5, 120.2, 120.4, 120.9, 122.01, 122.03, 123.6, 126.6,127.4, 127.6, 129.4, 134.2, 140.6, 140.95, 140.98, 141.0, 141.3, 141.6, 144.3, 150.7, 151.6, 152.1, 152.7; Orbitrap-MS: Calc. for $C_{44}H_{53}BO_2$ $[M]^+$ = 623.4169 (25%), 624.4133 (100%), 625.4167 (48%), 626.4200 (11%). Found: 623.4188 (24%), 624.4157 (100%), 625.4185 (45%), 626.4216 (10%).

4-Nitro-N,N-bis[4-(9,9,9',9'-tetra-n-propyl-9H,9'H-2,2'-bifluoren-7-yl)phenyl]aniline (**5**)

A mixture of **2** (2.65 g, 4.24 mmol), 4-bromo-*N*-[4-bromophenyl]-*N*-[4-nitrophenyl]aniline (0.761 g, 1.70 mmol), aqueous potassium carbonate (2 M, 8 mL), toluene (20 mL) and 2-propanol (4 mL) in a Schlenk tube was freeze-pump-thawed three times before backfilling with argon. *Tetrakis*[triphenylphosphine]palladium(0) (0.0981 g, 0.0849 mmol) was added to the reaction mixture, which was then stirred vigorously at 100 °C, under argon, for 20 h. After the reaction mixture was left to cool to room temperature, water (150 mL) and diethyl ether (100 mL) were added and the layers were separated. The aqueous layer was extracted with diethyl ether (100 mL) and the organic fractions were combined, washed with brine (100 mL), dried over magnesium sulfate, filtered, and the solvent removed to afford an orange solid. The residue was purified by column chromatography over silica using dichloromethane:light petroleum mixtures (0:1, 1:3, 2:3, 1:1) as eluent to afford **5** as an orange solid (1.98 g, 91%). mp = 186 °C; Found: C, 87.5; H, 7.3; N 2.2. $C_{94}H_{94}N_2O_2$ requires: C, 88.0; H, 7.4; N, 2.2%; λ_{max}(CH_2Cl_2)/nm 342sh (log ε/dm^3 mol^{-1} cm^{-1} 4.93), 361 (1.00), 424sh (2.19); ν_{max}/cm^{-1} 1495 (NO_2), 1464 (NO_2), 1392 (NO_2); δ_H(500 MHz, CD_2Cl_2): 0.64-0.83 (40 H, m, PrH), 2.00-2.17 (16 H, m, PrH), 7.11 and 8.10 (4H, AA'BB', TPAH), 7.31-7.38 (8H, m, TPAH and FlH), 7.41 (2H, d, J = 7.5, FlH), 7.64-7.72 (12H, m, TPAH and FlH), 7.76 (6H, d, J = 8.0, FlH), 7.79-7.85 (6H, m, FlH); δ_C(125 MHz, CD_2Cl_2): 14.8, 14.9, 17.8, 17.9, 43.27, 43.34, 56.0, 56.2, 119.2, 120.2, 120.4, 120.6, 120.7, 121.89, 121.98, 122.02, 123.6, 125.96, 126.33, 126.6, 126.7, 127.3, 127.4, 127.7, 129.0, 139.4, 139.5, 140.4, 140.90, 140.96, 140.97, 141.01, 141.2, 141.3, 145.3, 151.6, 152.1, 152.4, 152.5, 153.9; Orbitrap-MS: Calc. for $C_{94}H_{94}N_2O_2$ $[M]^+$ = 1282.7310 (98%), 1283.7343 (100%), 1284.7377 (50%), 1285.7410 (17%), 1286.7444 (4%). Found: 1282.7332 (97%), 1283.7367 (100%), 1284.7400 (50%), 1285.7434 (17%), 1286.7470 (4%).

*(1S,2R)-N-[4-(Bis{4-(9,9,9',9'-tetrapropyl-9H,9'H-(2,2'-bifluoren)-7-yl)phenyl}amino)phenyl]bicyclo[2.2.1]hept-5-ene-2-carboxamide (**M2**)*

Palladium on carbon (10% *w/w*, 0.167 g) was added to a solution of **5** (1.88g, 1.45 mmol) in chloroform (60 mL) and ethanol (20 mL). The mixture was purged with hydrogen for 5 min before being stirred in the dark overnight under hydrogen at room temperature. The reaction mixture was filtered through a Celite plug, which was washed with chloroform (100 mL). The filtrate was collected and the solvent removed to give crude amine as peach solid (≈2.14 g), which was used without further purification. (1*S*,4*R*)-Bicyclo[2.2.1]hepta-2,5-diene-2-carboxylic acid (0.20 g, 1.45 mmol, 97% *exo*) was added to a solution of the amine (≈1.84 g), *N*,*N*-dicyclohexylcarbodiimide (0.60 g, 2.90 mmol), 4-*N*,*N*-dimethylaminopyridine (0.36 g, 2.90 mmol) in freshly distilled dichloromethane (50 mL). The reaction mixture was stirred at room temperature for 16 h in the dark under argon atmosphere. The reaction mixture was diluted with dichloromethane (100 mL) and then washed with water (3 x 100 mL) followed by brine (100 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and then the solvent was removed to give a yellow solid. The residue was purified by column chromatography over silica using ethyl acetate:light petroleum spirit mixtures (0:1, 1:9, 3:17) as eluent to afford a yellow solid. The solid was recrystallised from a dichloromethane:light petroleum mixture to give **M2** as a pale yellow solid (0.445 g). The filtrate from the recrystallisation was also collected and the solvent removed. The residue was further purified using Chromatotron^{TM} chromatography loaded from dichloromethane and then using dichloromethane:light petroleum mixtures (0:1, 1:19, 3:17). The batches of pale yellow **M2** were combined to give (0.597 g, 35%). mp 190 °C; Found: C, 88.5; H, 7.7; N, 2.0. $C_{102}H_{104}N_2O$ requires: C, 89.2; H, 7.6; N, 2.0%; $\lambda_{max}(CH_2Cl_2)$/nm 302sh (log ε/dm^3 mol^{-1} cm^{-1} 4.71), 337sh (4.98), 369 (5.09); δ_H(500 MHz; CD_2Cl_2) 0.65-0.80 (40H, m, propylH), 0.83-0.87 (1H, m, NbH), 1.37-1.44 (2H, m, NbH), 1.76 (1H, d, J = 8.5, NbH), 2.00-2.13 (16H, m, PrH), 2.16-2.20 (1H, m, NbH), 2.97 (1H, brs, NbH), 3.06 (1H, br s, ring H), 6.17-6.22 (2H, m, NbH), 7.18 and 7.52 (4H, AA'BB', TPAH), 7.22 (4H, 1/2AA' BB', TPAH), 7.28 (1H, brs, NH), 7.30-7.37 (4H, m, FlH), 7.39-7.41 (2H, m, FlH), 7.61-7.65 (8H, m, TPAH and/or FlH), 7.66-7.70 (8H, m, TPAH and/or FlH), 7.74-7.77 (2H, m, FlH), 7.79-7.83 (6H, m, FlH); δ_C(125 MHz; CD_2Cl_2)

14.80, 14.84, 17.8, 17.9, 31.1, 42.3, 43.3, 43.4, 46.3, 46.7, 48.0, 56.0, 56.1, 120.2, 120.41, 120.43, 120.5, 121.4, 121.6, 121.97, 121.98, 123.6, 124.3, 126.0, 126.1, 126.5, 126.7, 127.4, 127.6, 128.3, 134.9, 136.1, 136.5, 139.0, 140.0, 140.3, 140.6, 140.9, 141.0, 141.3, 147.5, 151.6, 152.1, 152.34, 152.35, 174.1; Orbitrap-MS: Calc. for $C_{102}H_{104}N_2O$ $[M]^+$ = 1372.8143 (91%), 1373.8177 (100%), 1374.8210 (55%), 1375.8244 (20%), 1376.8277 (5%). Found: 1372.8164 (97%), 1373.8203 (100%), 1374.8237 (53%), 1375.8272 (19%), 1376.8307 (5%); PL: λ_{max} (toluene)/nm 423, 458sh. PLQY (sol., toluene) 71%. CV: $E_{1/2}^{ox}$ = 0.2 V *vs*. Fc/Fc$^+$.

*Poly[N-(4-{bis[4-(9,9,9',9'-tetra-n-propyl-9H,9'H-{2,2'-bifluoren}-7-yl)phenyl]amino}phenyl)-2,4-divinylcyclopentane-1-carboxamide] (**P2**)*

A solution of **M2** (0.452 g, 0.329 mmol) freshly distilled anhydrous tetrahydrofuran (7.5 mL) in a Schlenk tube was freeze-pump-thawed three times and backfilled with argon. The reaction vessel was covered with aluminium foil to protect the contents from light. Grubb's third generation catalyst (14.6 mg g, 16.5 μmol) in freshly distilled anhydrous tetrahydrofuran (0.5 mL) was added rapidly added to the stirred reaction mixture under argon. The reaction mixture was stirred at room temperature under argon for 1.75 h before being quenched with ethyl vinyl ether (0.3 mL). The reaction mixture was then dropped into methanol (100 mL). The resultant precipitate was collected via filtration and washed with methanol (3 × 10 mL). The solid was redissolved in dichloromethane (25 mL) and dropped into methanol (100 mL), and the precipitate was collected via filtration and washed with methanol (3 × 10 mL) before being dried under high-vacuum to give **P2** as a pale yellow-green solid (0.302 g, 68%). Found: C, 88.7; H, 7.6; N, 2.0. $C_{102}H_{104}N_2O$ (repeating unit) requires: C, 89.2; H, 7.6; N, 2.0%; λ_{max} (toluene/nm): 365, 340sh; δ_H(500 MHz, CD_2Cl_2): 0.48-0.80 (br, CpH and/or PrH), 1.00-1.35 (br, CpH), 1.45-1.80 (br, PrH), 1.80-2.20 (br, PrH), 2.20-2.55 (br, CpH), 2.55-2.90 (br, CpH), 2.90-3.35 (br, CpH), 5.05-5.70 (br, VinH), 6.85-7.83 (brm, FlH, TPAH and NH); GPC: $\overline{M}_w$ = 2.4×10^4, $\overline{M}_n$ = 1.8×10^4, Đ = 1.3; $TGA_{(5\%)}$ = 433 °C; PL: λ_{max} (toluene/nm) 441, 461sh; PL: λ_{max} (25 nm neat film) 450; PLQY (sol., toluene) 66%; PLQY (25 nm neat film) 12%; CV: $E_{1/2}^{ox}$ = 0.2 V *vs*. Fc/Fc$^+$.

*4-[7-(4,4''-Bis{[2-ethylhexyl]oxy}-{1,1':3',1''-terphenyl}-5'-yl)-9,9-di-n-propyl-9H-fluoren-2-yl]-N-[4-(7-{4,4''-bis[(2-ethylhexyl)oxy]-[1,1':3',1''-terphenyl]-5'-yl}-9,9-di-n-propyl-9H-fluoren-2-yl)phenyl]-N-[4-nitrophenyl]aniline (**6**)*

A mixture of 2-[7-(4,4''-bis{[2-ethylhexyloxy]-[1,1':3',1''-terphenyl]-5'-yl)-9,9-di-propyl-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[3] (2.10 g, 2.47 mmol), 4-bromo-*N*-[4-bromophenyl]-*N*-[4-nitrophenyl]aniline (0.369 g, 0.823 mmol), aqueous potassium carbonate (2 M, 2 mL) and toluene (5 mL) was degassed using three freeze-pump-thaw cycles before backfilling with argon. *Tetrakis*[triphenylphosphine]palladium(0) (0.142 g, 0.123 mmol) was added and the reaction mixture was stirred at 100 °C overnight under argon. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (100 mL) and distilled water (100 mL). The organic phase was collected and washed with water (3 × 50 mL). The aqueous fractions were combined and extracted with ethyl acetate (100 mL). The organic fractions were combined and washed with brine (100 mL), dried over anhydrous sodium sulfate, filtered and the solvent removed to leave a brown solid (2.16 g). The residue was purified using column chromatography over silica with dichloromethane:light petroleum mixtures as eluent (0:1, 1:4, 1:1) to yield **6** as a yellow solid (1.25 g, 86%). mp 168 °C; Found: C, 84.3, H, 8.1; N, 1.5. $C_{124}H_{142}N_2O_6$ requires: C, 84.8; H, 8.1; N, 1.6%; λ_{abs} (CH_2Cl_2)/nm: 253sh (log ε/M^{-1}cm^{-1}, 4.88), 282 (5.00), 332sh (4.92), 353 (5.00), 416 (4.45); ν_{max}/cm^{-1} 1584 (NO_2), 1287 (NO_2); δ_H(500 MHz; CD_2Cl_2) 0.63-0.80 (20H, m, PrH), 0.91-1.00 (24H, m, EHH), 1.29-1.58 (32H, m, EHH), 1.71-1.80 (4H, m, EHH), 2.04-2.14 (8H, m, PrH), 3.91-3.93 (8H, m, EHH), 7.03 (8H, 1/2AA'BB', SPH), 7.10 and 8.09 (4H, AA'BB', TPAH), 7.35 (4H, 1/2AA'BB', TPAH), 7.62-7.70 (12H, m, FlH and/or TPAH and/or BPH and/or SPH), 7.71-7.77 (10H, m, TPAH and/or BPH and/or FlH), 7.79 (4H, d, J = 1.5, BPH), 7.82-7.86 (4H, m, FlH); δ_C(125 MHz; CD_2Cl_2): 11.5, 14.4, 14.8, 17.9, 23.7, 24.5, 29.7, 31.1, 40.0, 43.3, 56.2, 71.2, 115.4, 119.2, 120.6, 120.7, 121.9, 122.4, 124.5, 124.7, 126.0, 126.3, 126.8, 127.3, 128.8, 129.0, 133.9, 139.4, 139.6, 140.7, 140.8, 140.9, 141.0, 142.5, 143.1, 145.4, 152.4, 152.5, 153.9, 159.9; Orbitrap-MS: Calc. for $C_{124}H_{142}N_2O_6$ $[M]^+$ = 1755.0862 (75%), 1756.0896 (100%), 1757.0930 (67%), 1758.0963 (29%), 1759.0997 (10%). Found: 1755.0897 (69%), 1756.0915 (100%), 1757.0962 (69%), 1758.0995 (30%), 1759.1067 (5%).

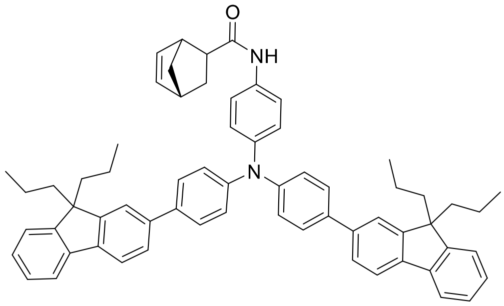
*(1S,2R)-N-[4-(Bis{4-[7-(4,4''-bis{[2-ethylhexyl]oxy}-{1,1':3',1''-terphenyl}-5'-yl)-9,9-di-n-propyl-9H-fluoren-2-yl]phenyl}amino)phenyl]bicyclo[2.2.1]hept-5-ene-2-carboxamide (**M3**)*

Palladium on carbon (0.165 g, 10% *w/w*) was added to a solution of **5** (1.25g, 0.713 mmol) in chloroform (60 mL) and ethanol (20 mL). The mixture was purged with hydrogen for 5 min before being left to stir in the dark overnight under hydrogen at room temperature. The reaction mixture was filtered through a Celite plug which was washed with chloroform (100 mL), and the filtrate was collected and the solvent removed to give the crude amine as brown solid (≈1.26 g), which was used without further purification. (1*S*,4*R*)-Bicyclo[2.2.1]hepta-2,5-diene-2-carboxylic acid (9.83 mg, 0.712 mmol, 97% *exo*) was added to a mixture of the amine (≈1.24 g), *N*,*N*-dicyclohexylcarbodiimide (0.293 g, 1.42 mmol), 4-*N*,*N*-dimethylaminopyridine (0.175 g, 1.42 mmol) and freshly distilled dichloromethane (15 mL). The reaction mixture was stirred for 16 h in the dark under argon at room temperature. The solvent was removed and the residue was redissolved in ethyl acetate (150 mL). The organic solution was washed with water (3 × 75 mL) and then brine (100 mL), dried over anhydrous sodium sulfate, filtered, and then the solvent was removed to give a brown oil. The residue was purified by column chromatography over silica using an ethyl acetate:light petroleum spirit mixture (1:4) as eluent to give a yellow solid (0.639 g). The solid was further purified using Chromatotron^{TM} chromatography loaded from diethyl ether and then using ethyl acetate:light petroleum mixtures (0:1, 1:19, 1:9) as eluent to yield **M3** as a pale yellow solid (0.450 g, 35%). mp 148 °C; Found: C, 85.5, H, 8.4, N, 1.5. $C_{132}H_{152}N_2O_5$ requires: C, 85.9; H, 8.3; N, 1.5%; $\lambda_{max}(CH_2Cl_2)$/nm 259sh (log ε/dm^3 mol^{-1} cm^{-1} 4.90), 285 (5.00), 327sh (4.76), 366 (4.94); δ_H(500 MHz; CD_2Cl_2) 0.69-0.80 (20H, m, PrH), 0.83-0.99 (25H, m, EHH and NBH), 1.33-1.60 (34H, m, EHH and NBH), 1.73-1.82 (4H, m, EHH), 2.00-2.14 (9H, m, PrH and NBH), 2.15-2.20 (1H, m, NBH), 2.97 (1H, brs, NBH), 3.06 (1H, brs, NBH), 3.90-3.96 (8H, m, EHH), 6.15-6.23 (2H, m, NBH), 7.04 (8H, 1/2AA’BB’, SPH), 7.18 and 7.52 (4H, AA’BB’, TPAH), 7.22 (4H, 1/2AA’BB’, TPAH), 7.30 (1H, s, NH), 7.58-7.66 (8H, m, FlH and/or TPAH and/or BPH and/or SPH), 7.66-7.72 (8H, m, FlH and/or TPAH and/or BPH and/or SPH), 7.72-7.75 (6H, m, FlH and/or TPAH and/or BPH and/or SPH), 7.76-7.85 (8H, m, FlH and BPH); δ_C(125 MHz; CD_2Cl_2) 11.5, 14.5, 14.9, 17.9, 23.7, 24.5, 29.7, 31.1, 40.0, 42.3, 43.3, 46.3, 46.7, 48.0, 56.1, 71.2, 115.4, 120.5, 120.6, 121.5, 121.6, 122.3, 124.3, 124.5, 124.7, 126.0, 126.1, 126.7, 128.4,128.8, 133.9, 134.9, 136.1, 136.5, 139.0, 140.1, 140.2, 140.7, 140.9, 142.5, 143.1, 143.9, 147.5, 152.36, 152.39, 159.9, 174.2; MALDI-TOF (DCBT) Calc. for $C_{132}H_{152}N_2O_5$: 1845.17 (69%), 1846.17 (100%), 1847.18 (73%), 1848.18 (36%), 1849.18 (13%). Found: 1844.78 (63%), 1845.79 (100%), 1846.78 (76%), 1847.78 (36%), 1848.77 (11%); PL: λ_{max}(toluene)/nm 431, 448sh. PLQY (sol., toluene) 70%. CV: $E_{1/2}^{ox} = 0.2$ V *vs*. Fc/ Fc^+.

Poly[N-(4-{bis[4-(7-{4,4''-bis[(2-ethylhexyl)oxy]-[1,1':3',1''-terphenyl]-5'-yl}-9,9-di-n-propyl-9H-fluoren-2-yl)phenyl]amino}phenyl)-2,4-divinylcyclopentane-1-carboxamide] ***(P3)***

A solution of **M3** (0.184 g, 0.100 mmol) and freshly distilled dry tetrahydrofuran (5 mL) in a Schlenk tube was freeze-pump-thawed three times and backfilled with argon. The reaction vessel was covered with aluminium foil to protect the contents from light. A solution of Grubb's third generation catalyst (4.41 mg, 4.99 μmol) in freshly distilled anhydrous tetrahydrofuran (1 mL) was added rapidly to the stirred reaction mixture. The reaction mixture was then stirred at room temperature in the dark under argon for 3.5 h before being quenched with ethyl vinyl ether (0.5 mL). The reaction mixture was added dropwise into methanol (40 mL). The resultant precipitate was collected at the filter and then washed with methanol (5 × 20 mL) to yield a green solid. The solid was redissolved in dichloromethane (5 mL) then added dropwise into methanol (40 mL). The resulting precipitate was collected at the filter and washed with methanol (5 × 20 mL) to yield a green solid. The solid was dissolved again in dichloromethane (5 mL), then the solution was pipetted into a flask of methanol (40 mL). The precipitate was filtered, and then washed with methanol (5 × 20 mL). Final purification was achieved by dissolving the solid in toluene (4 mL) and passing through a BIO-RAD SX1 Bio-beads^{TM} column (toluene) wrapped in foil using toluene as eluent to yield **P3** as a green solid (0.120 g, 65%). Found: C, 84.7; H, 8.25; N, 1.5. $C_{132}H_{152}N_2O_5$ (repeating unit) requires: C, 85.9; H, 8.3; N, 1.5%; λ_{max}(toluene)/nm: 324sh, 369; δ_H(500 MHz, CD_2Cl_2): 0.50-0.80 (brm, CpH and/or PrH), 0.80-1.25 (br, CpH and/or EHH), 1.25-1.55 (br, CpH and/or EHH) 1.60-1.80 (br, CpH and/or EHH), 1.85-2.15 (br, PrH), 2.15-2.50 (br, CpH), 2.50-2.85 (br, CpH), 2.85-3.30 (br, CpH), 3.75-3.94 (br, EHH), 5.00-5.65 (br, VinH), 6.75-7.85 (brm, BPH, SPH, FlH, TPAH and NH); GPC: $\bar{M}_w$ = 3.5×10^4, $\bar{M}_n$ = 2.5×10^4, Đ = 1.4; TGA$_{(5\%)}$ = 424 °C; PL: λ_{max} (toluene/nm) 440; PL: λ_{max} (41 nm neat film) 452. PLQY (sol., toluene) 57%; PLQY (41 nm neat film) 9%; CV: $E_{1/2}^{ox}$ = 0.3 V *vs*. Fc/Fc$^+$.

M1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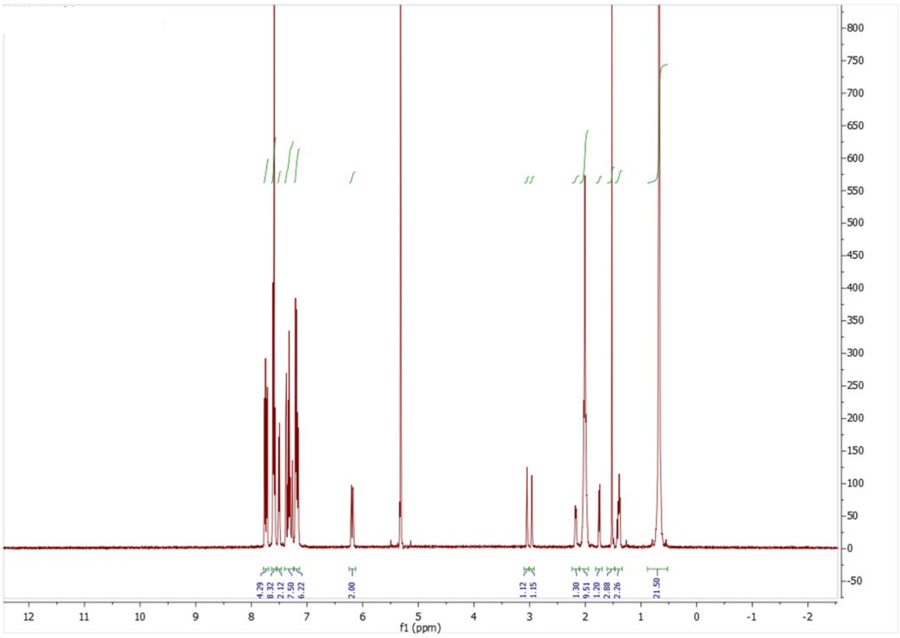
N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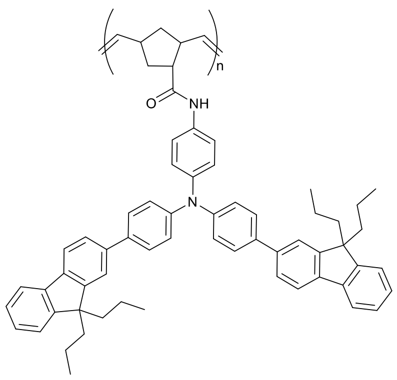
2.12
7.50
6.22
2.00
1.12
1.15
1.30
9.51
1.20
2.88
2.26
21.50
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

P1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NH
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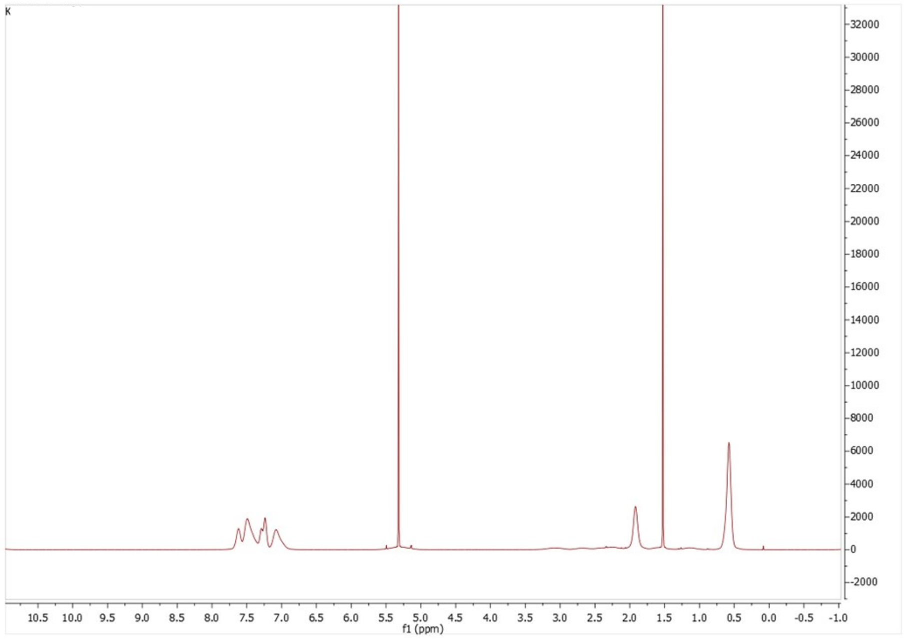
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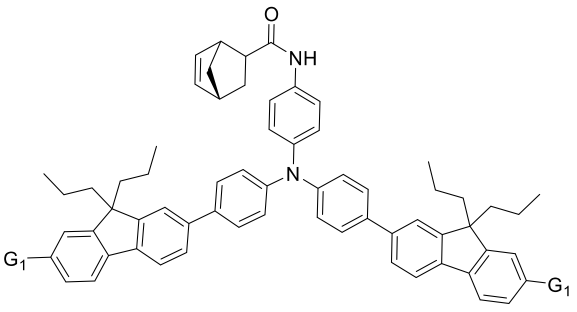
f1 (ppm)

M2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N
G1
G1

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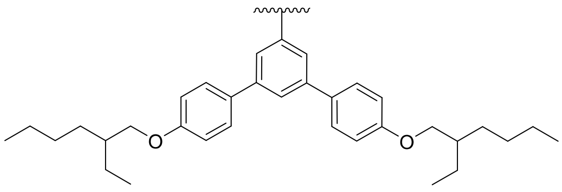
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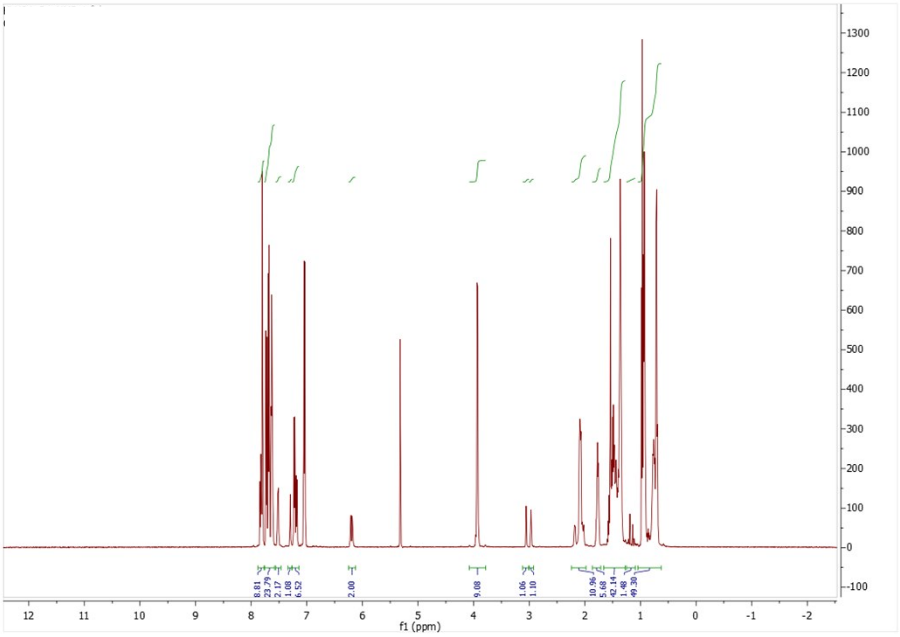
O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2.00
9.08
1.06
1.10
10.96
5.68
47.14
1.48
49.30
12
11
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5
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2
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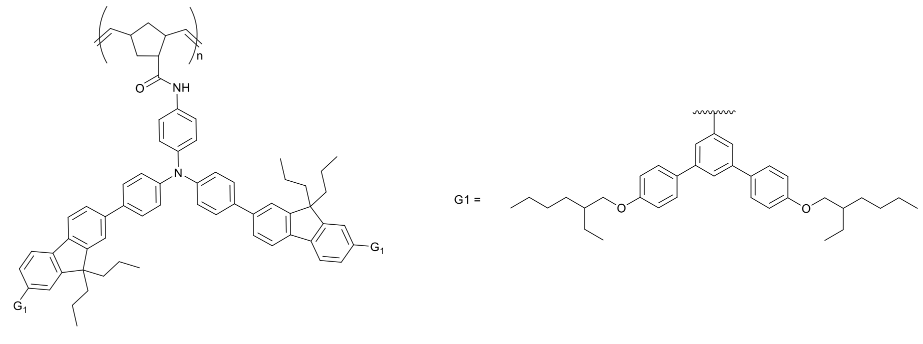
-1
-2
f1 (ppm)

P2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G1
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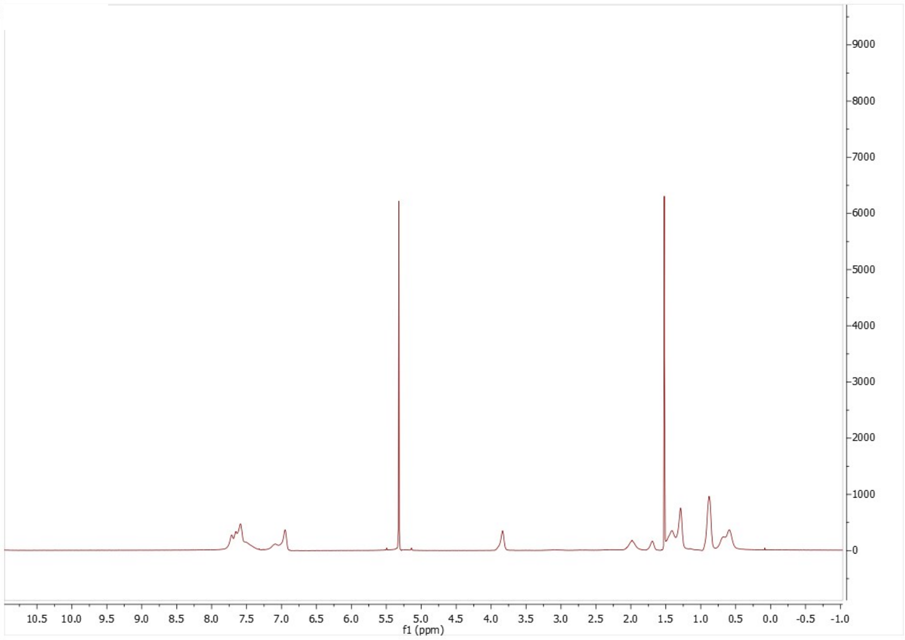
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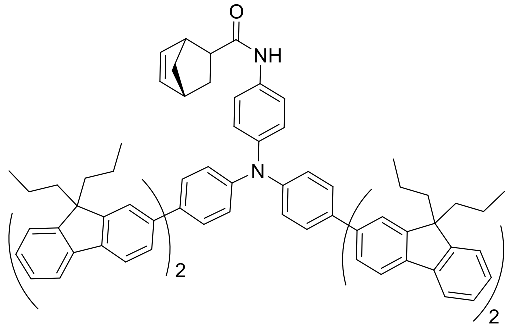
f1 (ppm)

M3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NH
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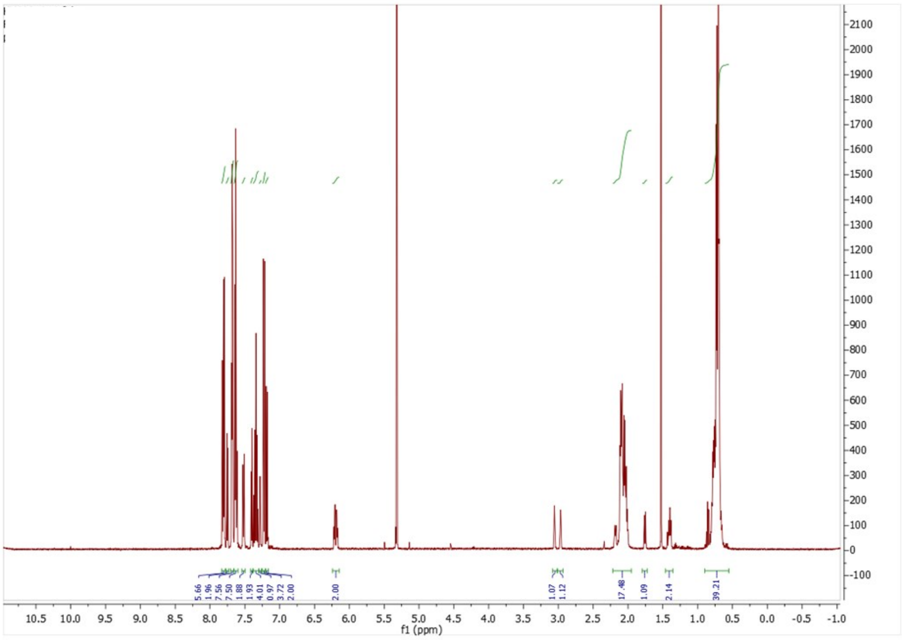
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2.14
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10.0
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9.0
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5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
2100
2000
1900
1800
1700
1600
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800
700
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500
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200
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0
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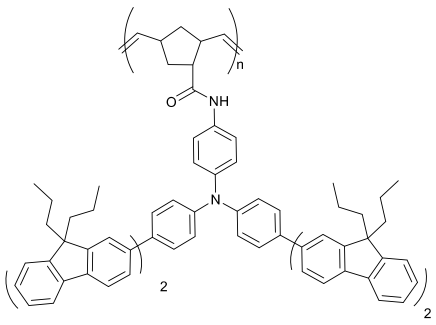
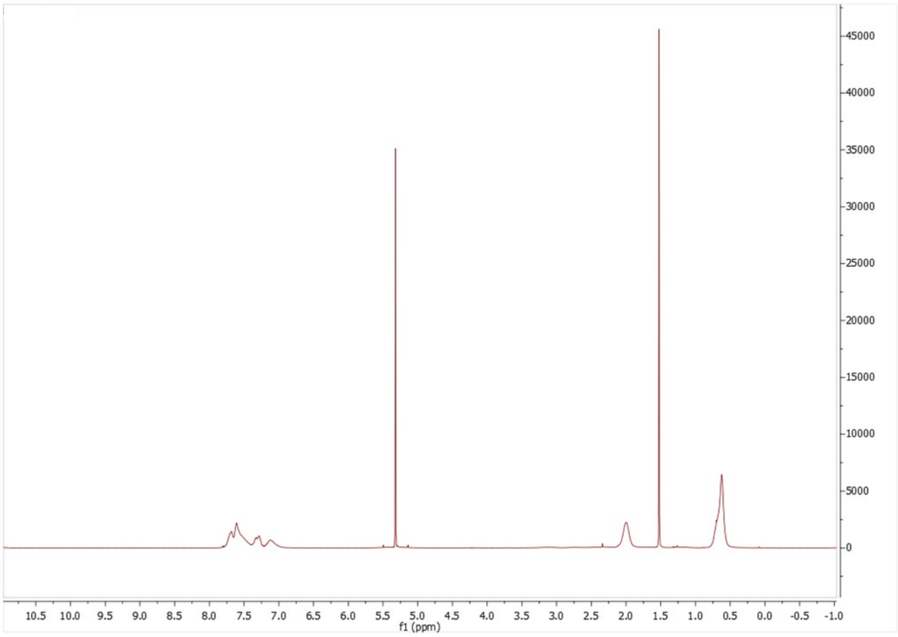
P3





References

1. B. T. Mayers and A. J. Fry, *Org. Lett.*, 2006, **8**, 411-414.

2. C. J. Kelly, A. Ghiorghis, Y. Qin, J. M. Kauffman, J. A. Novinski and W. J. Boyko, *J. Chem. Res. (S)*, 1999, 80-81.

3. Y. Geng, M. A. Ali, A. J. Clulow, S. Fan, P. L. Burn, I. R. Gentle, P. Meredith, P. E. Shaw, *Nat. Commun.*2015, **6**, 1-8.]