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Carbazole-based conjugated polymers with enhanced UV hardness: promising electron donor materials for stable organic solar cells

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Contents

Experimental

1. General

All solvents and reagents were purchased from commercial suppliers (Acros Organics, Sigma-Aldrich) and used as received or purified following the standard methods. All obtained compounds were purified to achieve the purity of at least 99.5% according to HPLC or NMR spectroscopy. The ^{1}H, ^{13}C and 2D NMR spectra in $CDCl_3$ solutions were obtained using Bruker AVANCE III 500 instrument.

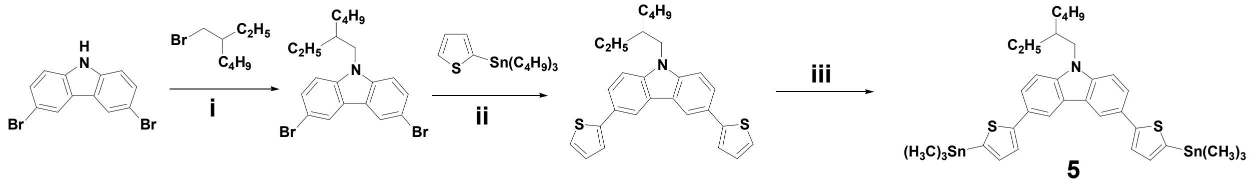
Molecular weight characteristics of conjugated polymers were obtained using Shimadzu LC20 instrument equipped with a Phenomenex Luna Phenogel 5u column (0.78×30 cm, 5-500 kDa).

Thermal gravimetry analysis was performed using a PerkinElmer Simultaneous Thermal Analyzer STA 8000 with a heating rate of 10ºC min^{-1} and nitrogen flow rate of 20 mL min^{-1}.

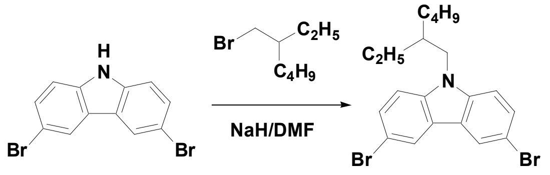
Cyclic voltammetry (CV) of the polymer films was performed using Elins P-30SM potentiostat at room temperature with a potential sweep rate of 50 mV s^{-1}. The CV measurements were performed for thin films of polymers deposited on glassy carbon disc electrode (working electrode) by drop casting from a mixture of polymers in 1,2-dichlorobenzene. The measurements were performed in a three-electrode electrochemical cell using 0.1M solution of Bu_4NPF_6 in dry acetonitrile as supporting electrolyte, platinum wire as a counter electrode and a silver wire immersed in a 0.01M solution of $AgNO_3$ in dry CH_3CN as a reference Ag^+/Ag electrode. Ferrocene was used as an internal standard. The electrolyte solution was purged with argon before the measurements.

PL spectra were measured using QE Pro High-Performance Spectrometer Ocean Insight fiber spectrometer and 405 nm diode laser (10 mW) as excitation source.

2. Synthesis of monomer 5.



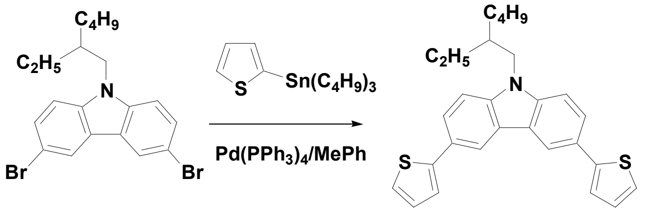
Scheme S1 *Reagents and conditions:* i, NaH/DMF; ii, $Pd(PPh_3)_4$/MePh; iii, 1) *n*-BuLi, 2) Cl-$Sn(CH_3)_3$



3,6-Dibromo-9-(2-ethylhexyl)-9*H*-carbazole

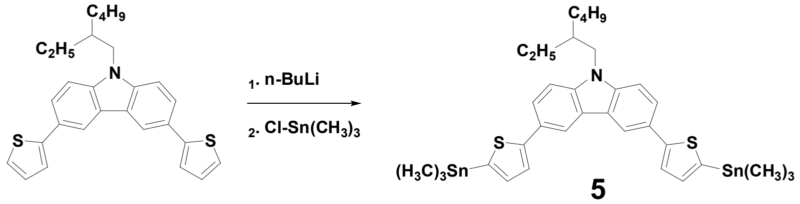
To a stirred solution of 3,6-dibromocarbazole (5 g, 15.385 mmol) in DMF (80 mL) at 0 °C NaH (0.905 g, 22.616 mmol, 60% in oil) was added. After gas evolution ceased, 2-ethylhexyl bromide (6.537 g, 33.847 mmol) was added, and the reaction mixture was stirred for 24 h at room temperature. Then 150 mL ice water was added, the mixture was stirred and diluted with 600 mL of ethyl acetate. The mixture was washed twice with NaCl solution (2 x 500 mL), dried over dry $MgSO_4$, filtered and evaporated. The residue was purified on a SiO_2 column with hexane/chloroform = 4:1 as eluent. Yield 6.5 g (96%) of a colorless oil. ^{1}H NMR (Fig. S4, 600

MHz, Chloroform-*d*) δ 8.16 (s, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 4.12 (dd, *J* = 7.1, 5.0 Hz, 2H), 2.12 – 1.91 (m, 1H), 1.44 – 1.14 (m, 7H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H).



9-(2-Ethylhexyl)-3,6-di(thiophen-2-yl)-9*H*-carbazole

A solution of 3,6-dibromo-9-(2-ethylhexyl)-9H-carbazole (4.1 g, 9.38 mmol) and 2-tributylstannylthiophene (10.50 g, 28.13 mmol) in dry toluene (100 mL) was purged with Argon for 20 min, then Pd(PPh$_3$)$_4$ (270 mg, 0.234 mmol) was added, and purging was continued for another 20 min. The reaction mixture was refluxed under an inert atmosphere for 36 h. After cooling, the reaction mixture was evaporated, the residue was purified by column chromatography on SiO$_2$ with a mixture of hexane/chloroform = 200:40 -> 150:75. The yield was 3.413 g (82%). ^{1}H NMR (Fig. S5, 600 MHz, Chloroform-*d*) δ 7.74 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.37 (d, *J* = 9.0 Hz, 4H), 7.27 (d, *J* = 5.0 Hz, 2H), 7.13 (dd, *J* = 4.9, 3.7 Hz, 2H), 4.16 (t, *J* = 7.6 Hz, 2H), 2.20 – 1.95 (m, 1H), 1.52 – 1.20 (m, 7H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (Fig. S6, 151 MHz, CDCl$_3$) δ 145.77, 141.01, 128.15, 126.01, 124.71, 123.85, 123.29, 122.24, 118.07, 109.59, 77.37, 77.16, 76.95, 47.73, 39.59, 31.13, 28.96, 24.52, 23.19, 14.20, 11.05.



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9-(2-Ethylhexyl)-3,6-bis(5-(trimethylstannyl)thiophen-2-yl)-9*H*-carbazole (5)

A solution of 9-(2-ethylhexyl)-3,6-di(thiophen-2-yl)-9*H*-carbazole (3.41 g, 7.69 mmol) in dry THF (180 mL) was cooled to -80 °C and *n*-BuLi solution (14.42 mL, 23.08 mmol, 1.6 M in hexane) was slowly added with good stirring, then warmed to -45 °C and stirred for another 1 h. After that, the reaction mixture was cooled again to -80 °C and a solution of Cl-SnMe$_3$ (4.60 g, 23.08 mmol) in THF (20 mL) was added. The reaction mixture was warmed to room temperature and stirred for 12 h. Then 200 mL of ethyl acetate were added and the mixture was washed with 200 mL of water. The organic layer was dried with MgSO$_4$, filtered and evaporated. The residue was recrystallized from hexane with heating. Yield 5.1 g (86%) of a light-gray substance. ^{1}H NMR (Fig. S7, 400 MHz, Chloroform-*d*) δ 8.37 (s, 2H), 7.76 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.50 (d, *J* = 3.2 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 3.3 Hz, 2H), 4.18 (dd, *J* = 7.2, 3.2 Hz, 2H), 2.18 – 1.96 (m, 1H), 1.49 – 1.23 (m, 7H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.45 (m, 18H).

3. Synthesis of polymers P1-P6

Stannane monomer **1,2** or **4** (0.214 mmol) and bromide **3** or **4** (0.214 mmol) were introduced into a degassed and argon-filled round-bottom three-necked 50 mL flask equipped with a reflux condenser and a thermometer. Anhydrous toluene (15 ml), tris(dibenzylidenacetone)dipalladium(0) (5 mg) and tri(*o*-tolyl)phosphine (12 mg) were added to the monomers in a flow of argon. The reaction flask was cooled down in liquid nitrogen, deaerated in vacuum, filled with argon and warmed up to the room temperature. This procedure was repeated three times to remove traces of oxygen. The flask was then immersed in an oil bath and heated at reflux for 5 hours. The molecular weight characteristics of the formed polymer were monitored every 20 min by analytical gel-permeation chromatography (GPC). When the polymer starts to precipitate or growth of polymer chains was self-terminated or the appropriate molecular weights were reached, 2-(trimethylstannyl)thiophene (0.75 mmol; 0.18 g) was added and heating at reflux was continued for 1 h. Afterwards, 2-bromothiophene (0.9 mmol) was added to the mixture and it was heated at reflux for another hour. Then the reaction mixture was cooled down to room temperature and the polymer was precipitated by addition of 50 mL of acetone. The precipitate was collected by filtration and then subjected to Soxhlet extractions with acetone, heptane, dichloromethane, chlorobenzene and also 1,2-dichlorobenzene if chlorobenzene did not extract the material effectively due to the limited solubility. Subsequently, the chlorobenzene and 1,2-dichlorobenzene (if any) fractions were concentrated to the volume of ca. 20 mL, treated with 3-mercaptopropionic acid for 3 hours and precipitated again with acetone (≈30 mL). The precipitate was collected by filtration and dried in vacuum. The total yield of the purified polymers **P1-P6** was 70-90%.

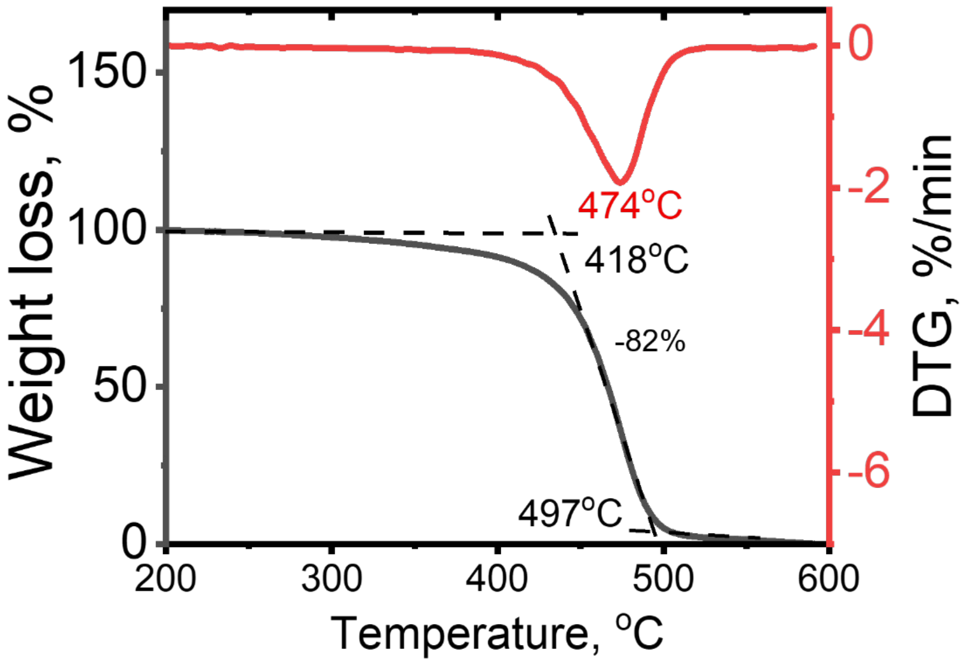

Figure S1. Thermogram of polymer **P1** (heating rate 10 K min^{-1}, in an inert N_2 atmosphere)

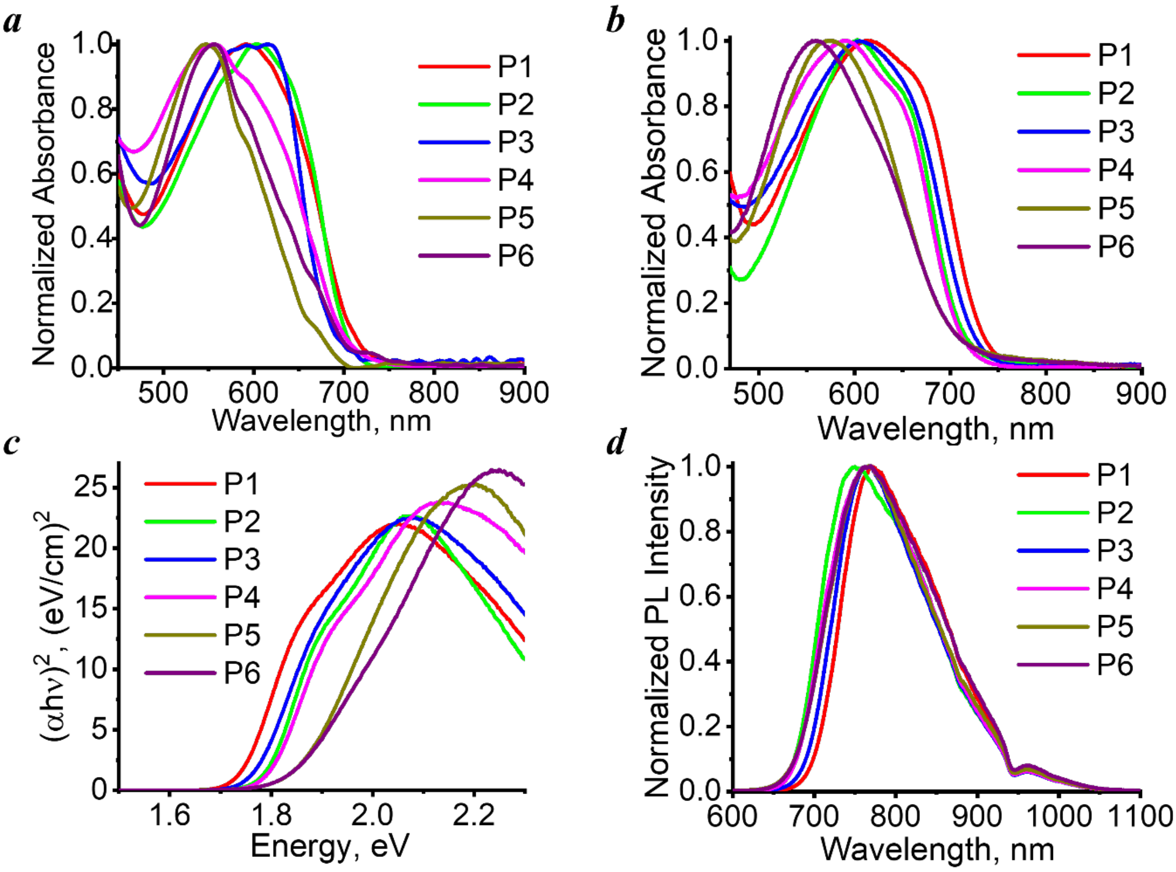

Figure S2. Absorption spectra of polymers **P1-P6** recorded in chlorobenzene (**P1**, **P3-P6)** or 1,2-dichlorobenzene (**P2**) (a) and in thin films (b). Tauc plots for **P1-P6** polymer films (c). Photoluminescence spectra of polymers **P1-P6** in thin films (d).

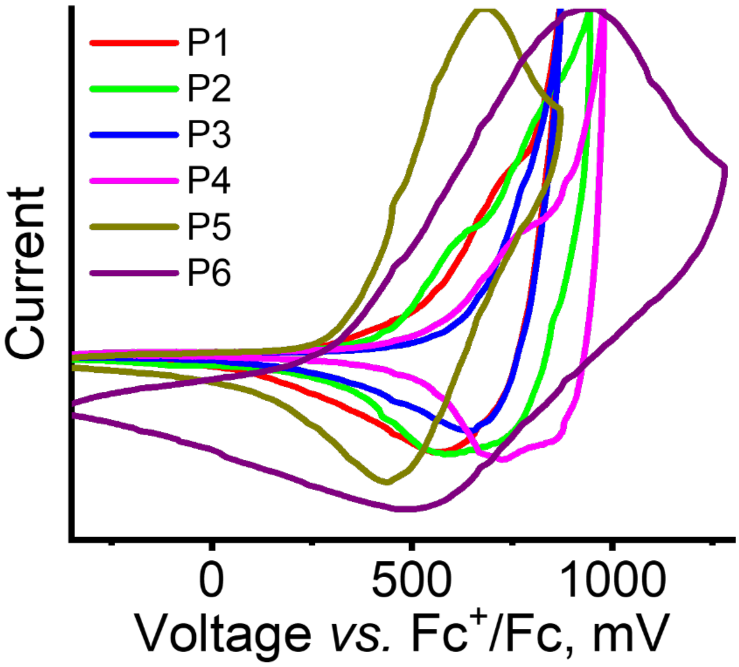

Figure S3. Cyclic voltammograms of thin films of polymers **P1-P6**

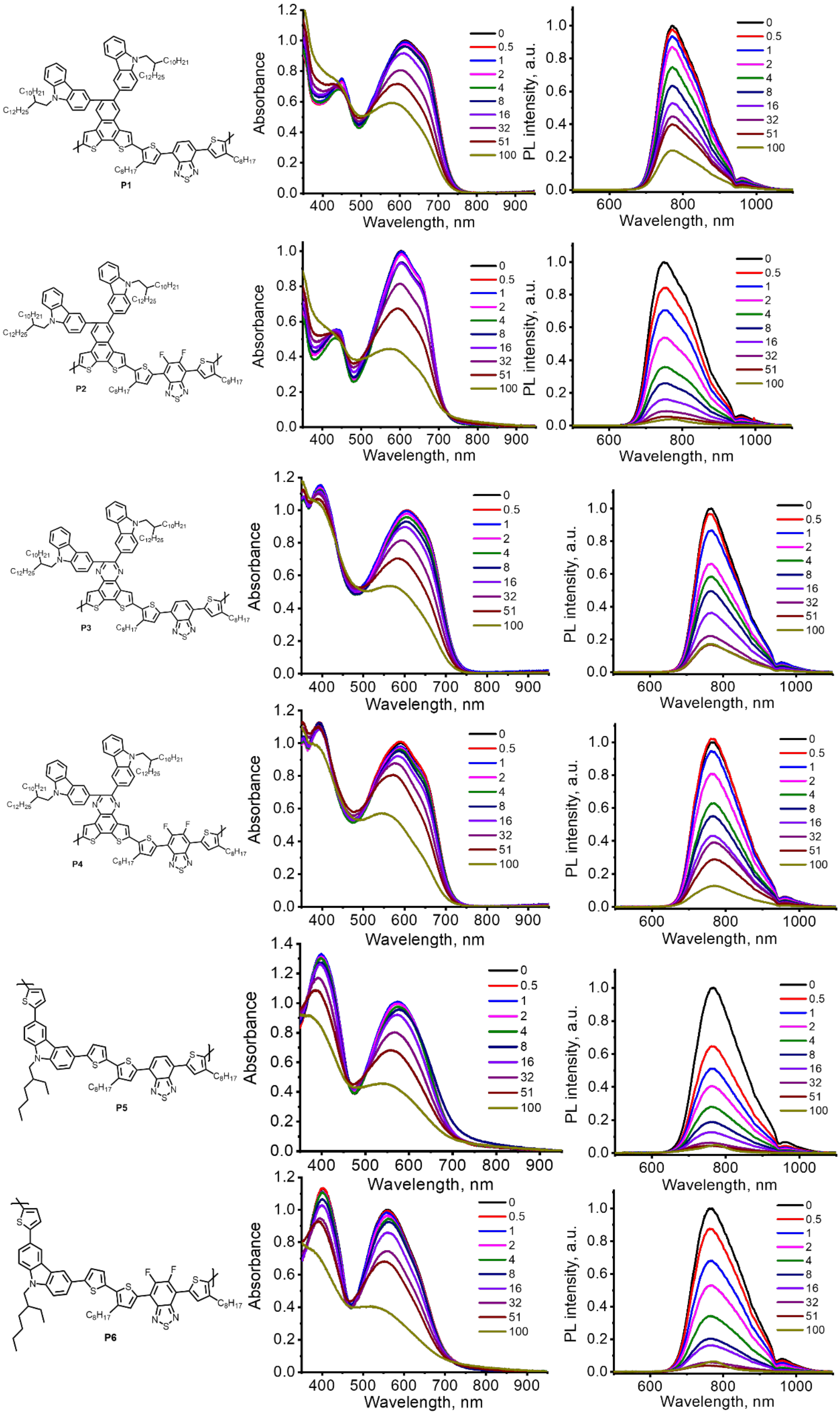

Figure S4. Molecular structures of the polymers and the dynamics of their UV-vis (center) and PL (right column) spectra under UV light exposure

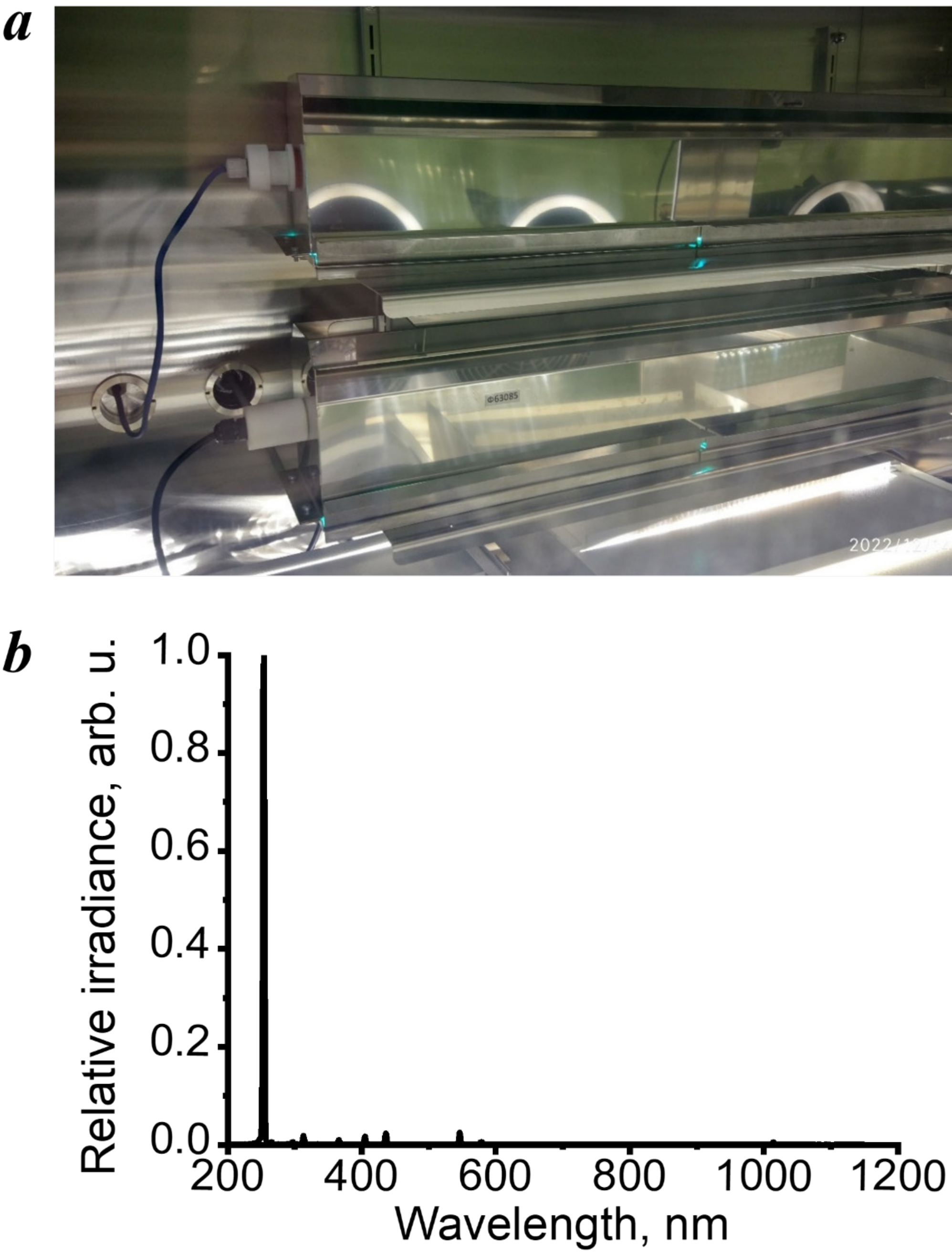

Figure S5. Photograph of the experimental setup: two UV lamps in metal shielding are placed inside the glove box (a) and emission spectrum of the lamp measured in 200-1150 nm range (b)

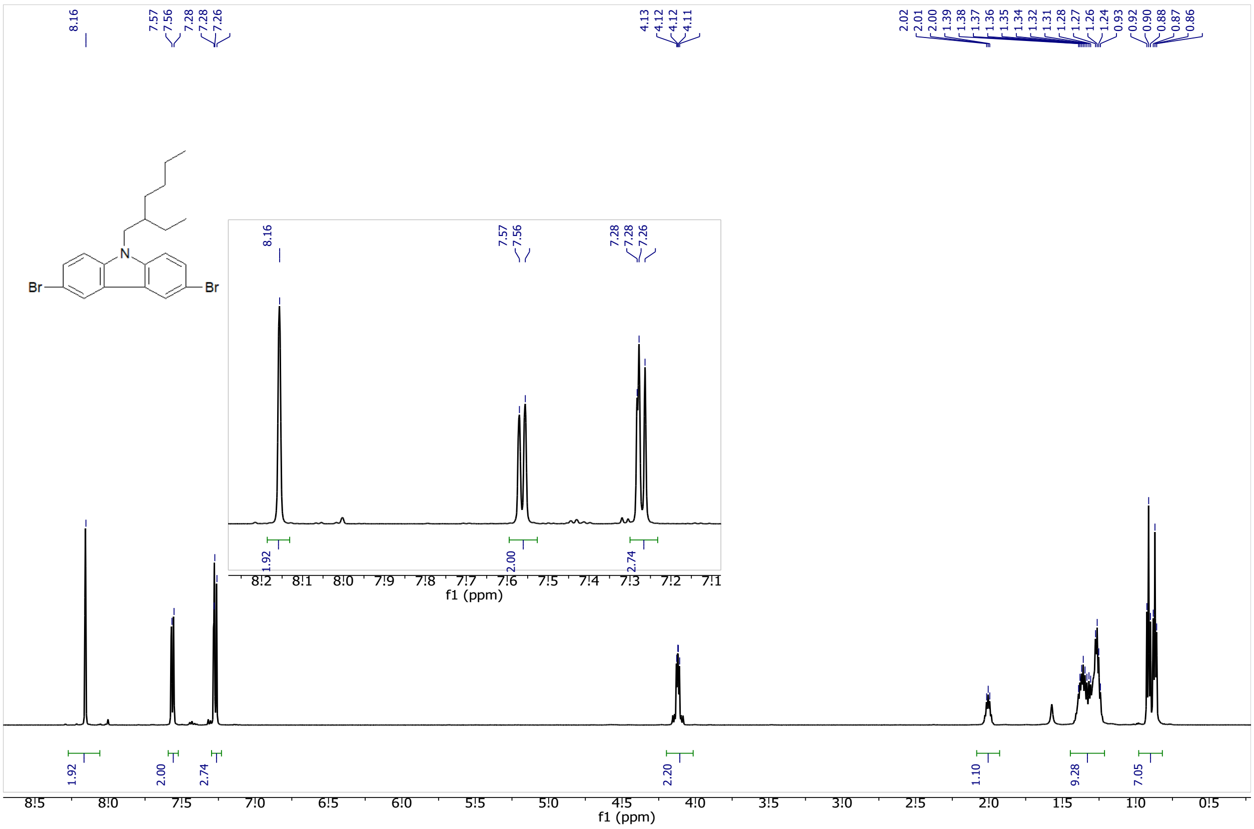

Figure S6. ^{1}H NMR spectrum of 3,6-dibromo-9-(2-ethylhexyl)-9*H*-carbazole

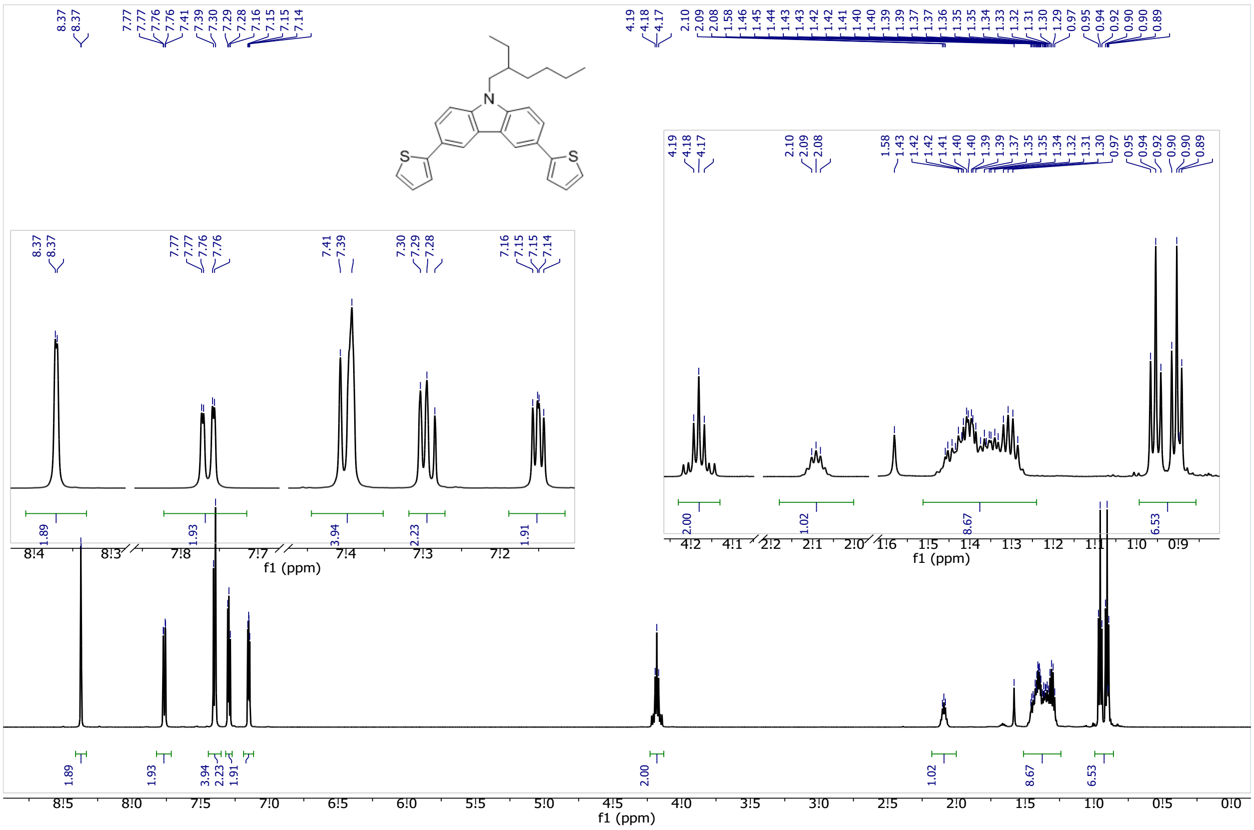

Figure S7. ^{1}H NMR spectrum of 9-(2-ethylhexyl)-3,6-di(thiophen-2-yl)-9*H*-carbazole

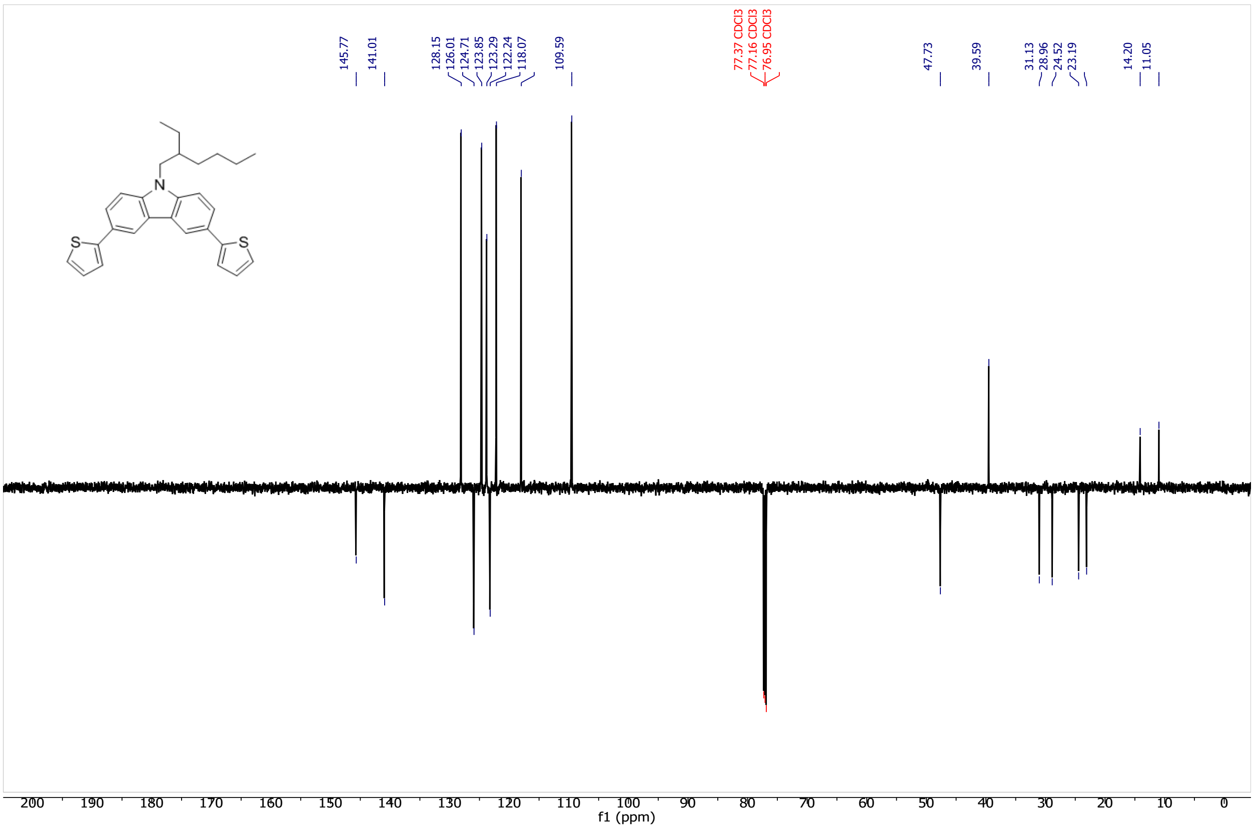

Figure S8. ^{13}C DEPT-135 NMR spectrum of 9-(2-ethylhexyl)-3,6-di(thiophen-2-yl)-9*H*-carbazole

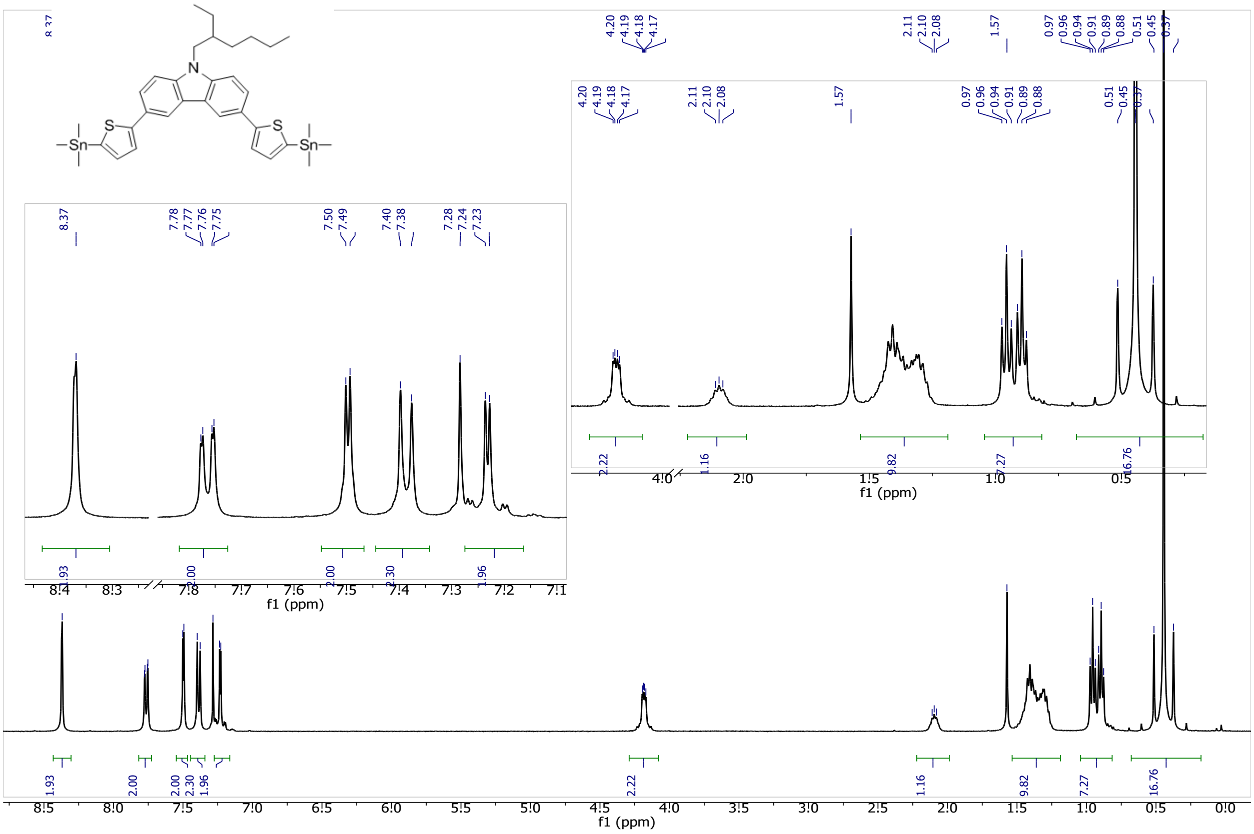

Figure S9. ^{1}H NMR spectrum of **3**