Electronic Supplementary Material (ESI) for RSC Advances.

D-π-A-π-D-type low band gap diketopyrrolopyrrole based small molecules containing ethynyl-linkage: synthesis and photovoltaic properties

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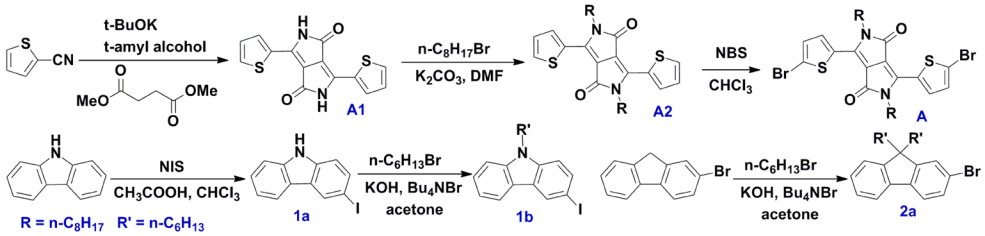
Supporting information

Table of contents

1. Synthetic procedures

Reagent and materials

All reagents were obtained from commercial suppliers and used as received unless specified. Tetrahydrofuran (THF) and toluene were dried by distillation over Na/benzophenone under nitrogen atmosphere prior to use. All reactions were performed under nitrogen atmosphere with the use of standard Schlenk techniques.



3,6-Dithien-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (A1): Potassium tert-butylate (4.00 g, 35.7 mmol) was added to a round flask under nitrogen (N_2). Then a solution of t-amyl alcohol (25 mL) and 2-thiophenecarbonitrile (3.27 g, 30.0 mmol) was injected by a syringe one portion. After the mixture was warmed up to 100 °C, a solution of dimethyl succinate (1.46 g, 10.0 mmol) in t-amyl alcohol (8 mL) was dropwised slowly. The reaction mixture was kept at 100 °C for about 1 h, and then the byproduct of methanol was distilled off and the reaction was kept for 2 h. After the mixture was cooled to 60 °C, the mixture was diluted with 50 mL of methanol and neutralized with acetic acid. The suspension was filtered, the purple filter cake was washed by hot methanol and water and dried in vacuum. The crude product (2.42 g, 76%) could be used directly without further purification.

3,6-Dithien-2-yl-2,5-di-n-octyl-pyrrolo[3,4-c]pyrrole-1,4-dione (A2): A solution of compound **A1** (0.30 g, 1.0 mmol) and anhydrous K_2CO_3 (0.41 g, 3.0 mmol) in 10 ml anhydrous N,N-dimethylformamide (DMF) was heated to 60 °C and stirred for 1 h under N_2. Then n-octylbromide (0.58 g, 3.0 mmol) was added to the mixture. The reaction mixture was further stirred at 60 °C for 18 h. After being cooled to room temperature, 40 mL of distilled water was poured into the system, and the resulting suspension was stirred at room temperature for 1 h. The suspension was filtered and the purple filter cake was washed with distilled water and methanol. The crude product was purified by silica column chromatography using dichloromethane (CH_2Cl_2) as eluent to get the final product as a dark purple crystalline solid (399 mg, 76%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.93 (d, J = 4.0 Hz, 2H), 7.64 (d, J = 4.0 Hz, 2H), 7.29 (d, J = 4.0 Hz, 2H), 4.07 (m, 4H), 1.78-1.71 (m, 4H), 1.44-1.37 (m, 4H), 1.36-1.31 (m, 16H), 0.87 (t, J = 8.0 Hz, 6H).

3,6-Bis(5-bromothiophen-2-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (A): To a solution of compound **A2** (525 mg, 1.0 mmol) in $CHCl_3$ (35 mL), NBS (356 mg, 2.0 mmol) was added. The reaction solution was stirred at room temperature for 5 h in dark. The organic solvent was removed under reduced pressure. The residue was purified by silica column chromatography using hexane/CH_2Cl_2 (v:v, 1:9) as eluent to get a purple solid (1.09 g, 80%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.67 (d, J = 4.0 Hz, 2H), 7.24 (d, J = 4.0 Hz, 2H), 3.98 (t, J = 8.0 Hz, 4H), 1.75-1.67 (m, 4H), 1.46-1.37 (m, 4H), 1.32-1.27 (m, 16H), 0.87 (t, J = 8.0 Hz, 6H).

3-Iodo-9H-carbazole (1a): To a solution of carbazole (836 mg, 5.0 mmol) in 50 mL glacial acetic acid/$CHCl_3$ (v:v, 1:1), NIS (1.13 g, 5.0 mmol) was added. The solution was stirred at room temperature overnight in dark. Then the mixture was poured into water (200 mL). The precipitate was filtered. The filter cake was dissolved with ethyl acetate, the organic solution was washing with saturated Na_2CO_3 and water and dried over anhydrous Na_2SO_4. The organic solvent was removed under reduced pressure. The residue was purified by silica column chromatography using petroleum ether/CH_2Cl_2 (v:v, 3:1) as eluent to get **1a** as a white solid (1.47 g, 80%). M.p.: 194-196 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.38 (d, J = 4.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.66 (m, 1H), 7.41-7.44 (m, 2H), 7.21-7.27 (m, 2H).

9-Hexyl-3-iodo-9H-carbazole (1b): A solution of compound **1a** (1.17 g, 4.0 mmol), Bu_4NBr (332 mg, 0.40 mmol), KOH (448 mg, 8.0 mmol) and n-hexylbromide (0.85 mL, 6.0 mmol) in acetone (15 mL) was refluxed for 4 h. After being cooled to room temperature, the mixture was poured into water. The precipitate was filtered by filtration and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether as the eluent to get compound **1b** as a colorless oil (1.39 g, 92%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 8.55 (s, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.45-7.49 (m, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 4.36 (t, *J* = 6.0 Hz, 2H), 1.72 (t, *J* = 8.0 Hz, 2H), 1.22-1.18 (m, 6H), 0.80-0.70 (m, 3H).

9-Hexyl-3-(2-(trimethylsilyl)ethynyl)-9H-carbazole (1c): Compound **1b** (1.32 g, 3.5 mmol), $Pd(PPh_3)_2Cl_2$ (140 mg, 0.20 mmol), CuI (38 mg, 0.20 mmol) and trimethylsilylacetylene (0.57 mL, 4.4 mmol) were added to the mixture solution of Et_3N (35 mL) and THF (25 mL) under N_2. The mixture was refluxed for 24 h. After being cooled to room temperature, the organic solvent was evaporated under reduced pressure. The crude product was purified by silica column chromatography using petroleum ether/CH_2Cl_2 (v:v, 20:1) as eluent to get **1c** as a yellow oil (583 mg, 48%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 8.34 (s, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 2H), 7.46-7.53 (m, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 4.39 (t, *J* = 8.0 Hz, 2H), 1.75 (t, *J* = 8.0 Hz, 2H), 1.19-1.27 (m, 6H), 0.81 (t, *J* = 8.0 Hz, 3H), 0.26 (s, 9H).

2-Bromo-9,9-dihexyl-9H-fluorene (2a): A solution of Compound **1** (1.17 g, 4.0 mmol), Bu_4NBr (332 mg, 0.4 mmol), KOH (448 mg, 8.0 mmol) and n-hexylbromide (0.85 mL, 6.0 mmol) in acetone (15 mL) was refluxed for 4 h. After cooling to room temperature, the reaction mixture was poured into water (200 mL) and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by silica column chromatography with petroleum ether as eluent to get compound **2a** as a yellow oil (1.65 g, 79%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.82 (m, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.52-7.50 (m, 1H), 7.44-7.42 (m, 1H), 7.36-7.32 (m, 2H), 2.01-1.96 (m, 4H), 1.07-0.98 (m, 12H), 0.72 (t, *J* = 8.0 Hz, 6H), 0.46-0.44 (m, 4H).

(2-(9,9-Dihexyl-9H-fluoren-2-yl)ethynyl)trimethylsilane (2b): Compound **2a** (1.65 g, 4.0 mmol), $Pd(PPh_3)_2Cl_2$ (140 mg, 0.20 mmol), CuI (38.0 mg, 0.20 mmol) and trimethylsilylacetylene (0.57 mL, 4.4 mmol) were added to a solution of Et_3N (35 mL) and THF (25 mL) under N_2. The mixture was refluxed for 24 h. After cooling to room temperature, the mixture was filtered and the organic solvent was removed under reduced pressure. The crude product was purified by silica column chromatography with petroleum ether/CH_2Cl_2 (v:v, 20:1) as eluent to get **2b** as a yellow oil (1.50 g, 88%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.60-7.68 (m, 2H), 7.43-7.47 (m, 2H), 7.31-7.33 (m, 3H), 1.94 (t, *J* = 8.0 Hz, 4H), 0.74-1.13 (m, 18H), 0.53-0.59 (m, 4H), 0.28 (s, 9H).

9-Hexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (1): A solution of compound **1b** (377 mg, 1.0 mmol), bis(pinacolato)diboron (278 mg, 1.10 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol), PPh_3 (10 mg, 0.04 mmol) and KOAc (147 mg, 1.50 mmol) in toluene (20 mL) was refluxed for 24 h under N_2. After being cooled to room temperature, the mixture was filtered and the filtrate was concentrated under reduced pressure. The crude product was purified by silica column chromatography using petroleum ether/ethyl acetate (v:v, 10:1) as eluent to give **1** as a colorless oil (211 mg, 60%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H) 8.13 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H) 7.47-7.43 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.25-7.21 (m, 1H), 4.27 (t, *J* = 8.0 Hz, 2H), 1.87-1.79 (m, 2H), 1.39 (s, 12H), 1.35-1.30 (m, 2H), 1.28-1.25 (m, 4H), 0.84 (t, *J* = 8.0 Hz, 3H).

2-(9,9-Dihexyl-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2): A solution of compound **2a** (412 mg, 1.0 mmol), bis(pinacolato)diboron (278 mg, 1.1 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol), PPh_3 (10.0 mg, 0.04 mmol) and KOAc (147 mg, 1.5 mmol) in toluene (20 mL) was refluxed for 24 h under N_2. After being cooled to room temperature, the mixture was filtered and the filtrate was concentrated by reduced pressure. The crude product was purified by silica column chromatography using petroleum ether/ethyl acetate (v:v, 12:1) as eluent to

give **2** as a colorless oil (258 mg, 76%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 2H) 7.66 (s, 2H), 7.44 (s, 1H), 7.34 (s, 2H), 1.97 (s, 4H), 1.32 (s, 12H), 0.97 (s, 12H), 0.71 (s, 6H), 0.44 (s, 4H).

3-Ethynyl-9-hexyl-9H-carbazole (3): Compound **1c** (580 mg, 1.67 mmol) and K_2CO_3 (2.31 g, 16.7 mmol) were added to a solution of CH_3OH (5 mL) and THF (5 mL). The reaction mixture was stirred at room temperature for 3 h. The organic solvent was removed under reduced pressure, the crude product was purified by silica column chromatography with petroleum ether/CH_2Cl_2 (v:v, 20:1) as eluent to give **3** as a light yellow oil (443 mg, 96%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.57 (dd, J_1 = 8.5 Hz, J_1 = 1.5 Hz, 1H), 7.48-7.44 (m, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.25-7.21 (m, 1H), 4.23 (t, J = 8.0 Hz, 2H), 3.05 (s, 1H), 1.85-1.78 (m, 2H), 1.36-1.23 (m, 6H), 0.84 (t, J = 6.0 Hz, 3H).

2-Ethynyl-9,9-dihexyl-9H-fluorene (4): Compound **2b** (861 mg, 2.0 mmol) and K_2CO_3 (2.76 g, 20 mmol) were added to a solution of CH_3OH (5 mL) and THF (5 mL). The reaction solution was stirred at room temperature for 5 h. After the organic solvent was evaporated, the crude product was purified by silica column chromatography with petroleum ether as eluent to give **4** as a light yellow oil (602 mg, 84%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69-7.67 (m, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.48-7.46 (m, 2H), 7.35-7.32 (m, 3H), 3.13 (s, 1H), 1.96-1.92 (m, 4H), 1.13-1.08 (m, 4H), 1.03-1.02 (m, 8H), 0.76 (t, J = 8.0 Hz, 6H), 0.60-0.57 (m, 4H).

2. ^{1}H-NMR and ^{13}C-NMR spectra

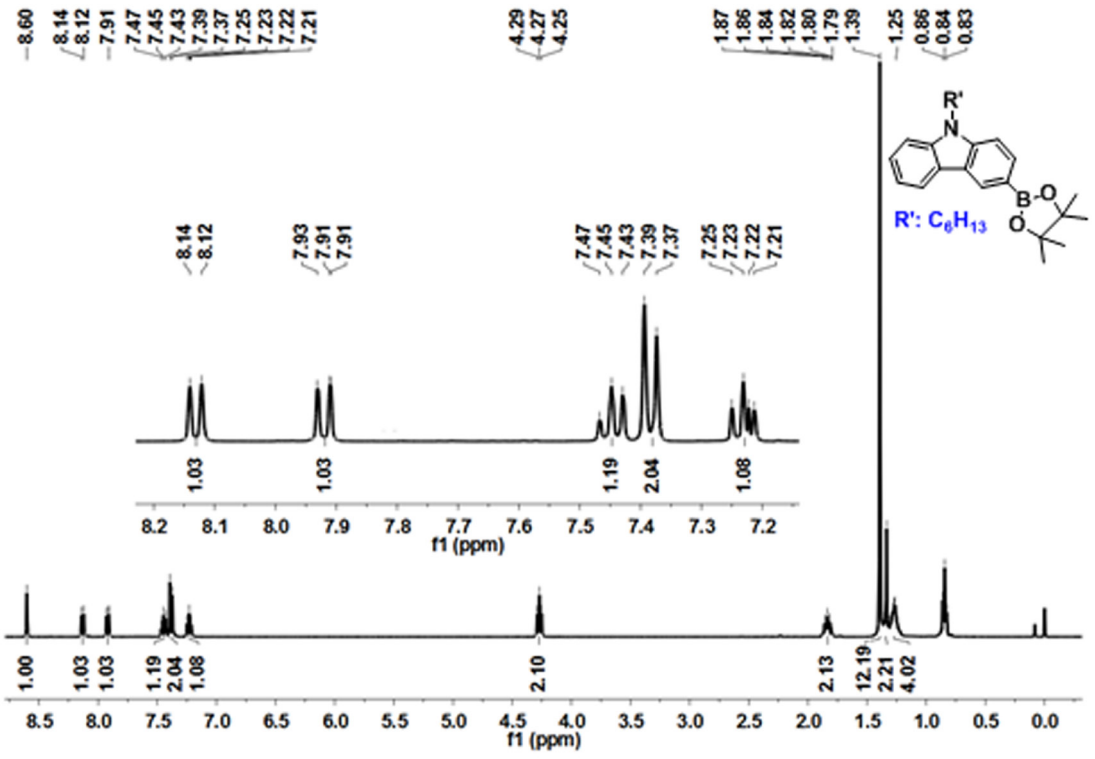


Fig. S1 ^{1}H-NMR of compound **1** in $CDCl_3$.

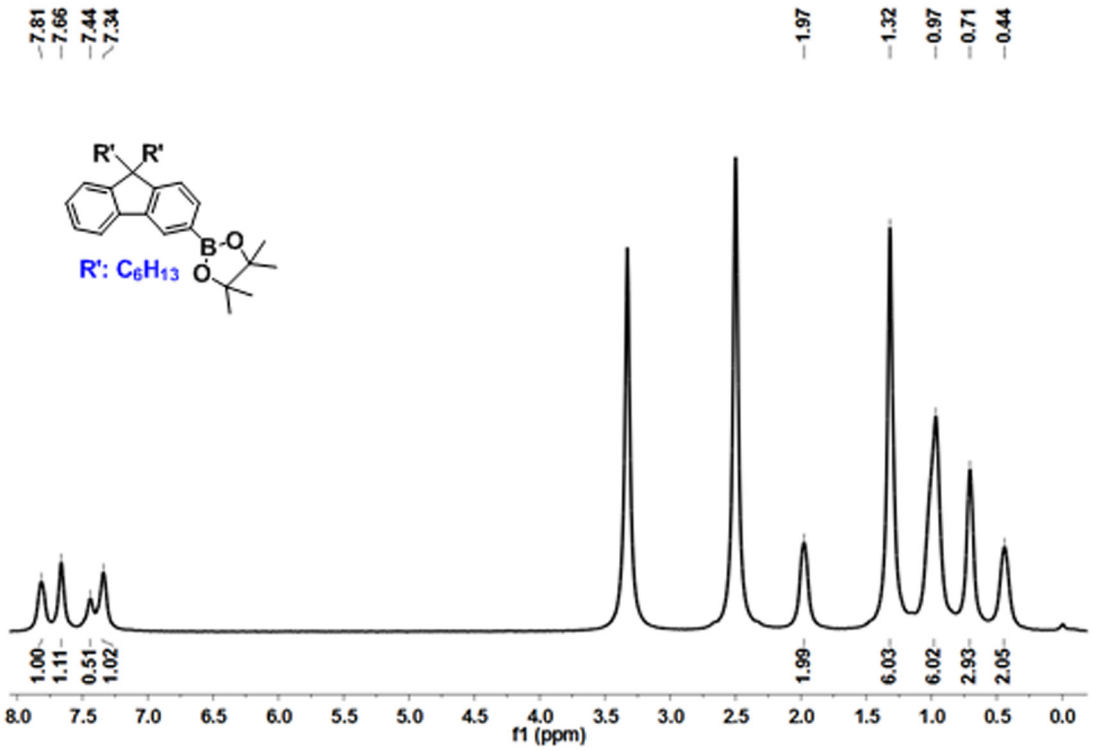


Fig. S2 ^{1}H-NMR of compound **2** in $CDCl_3$.

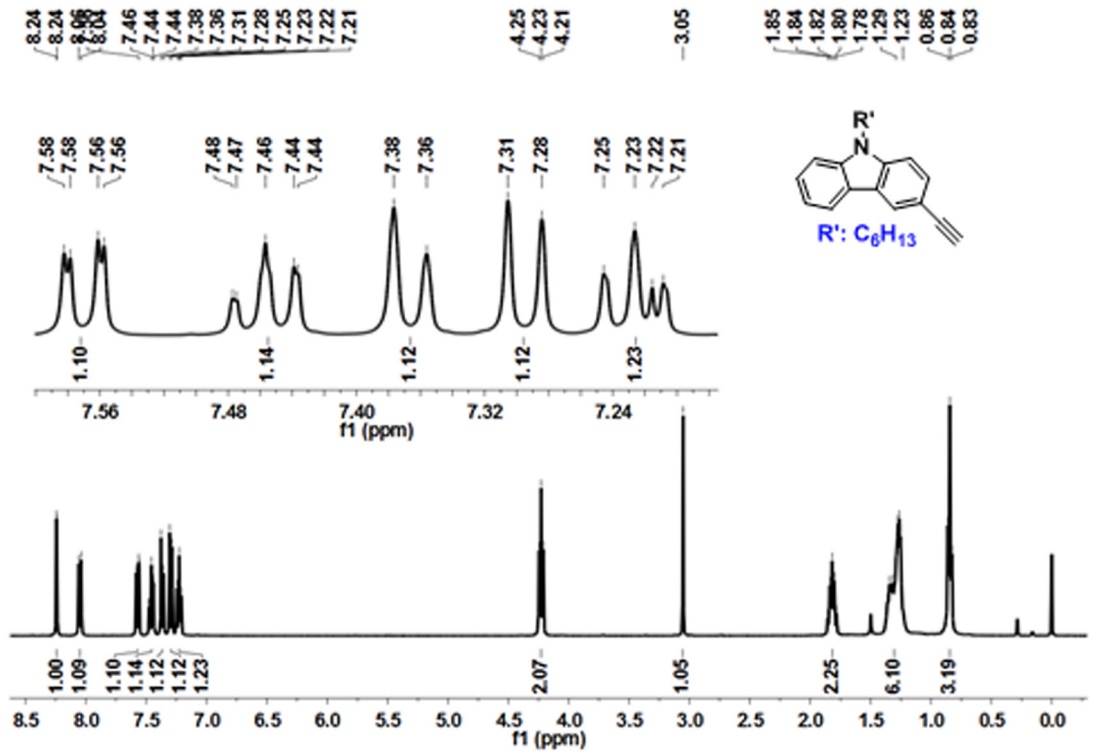


Fig. S3 ^{1}H-NMR of compound **3** in $CDCl_3$.

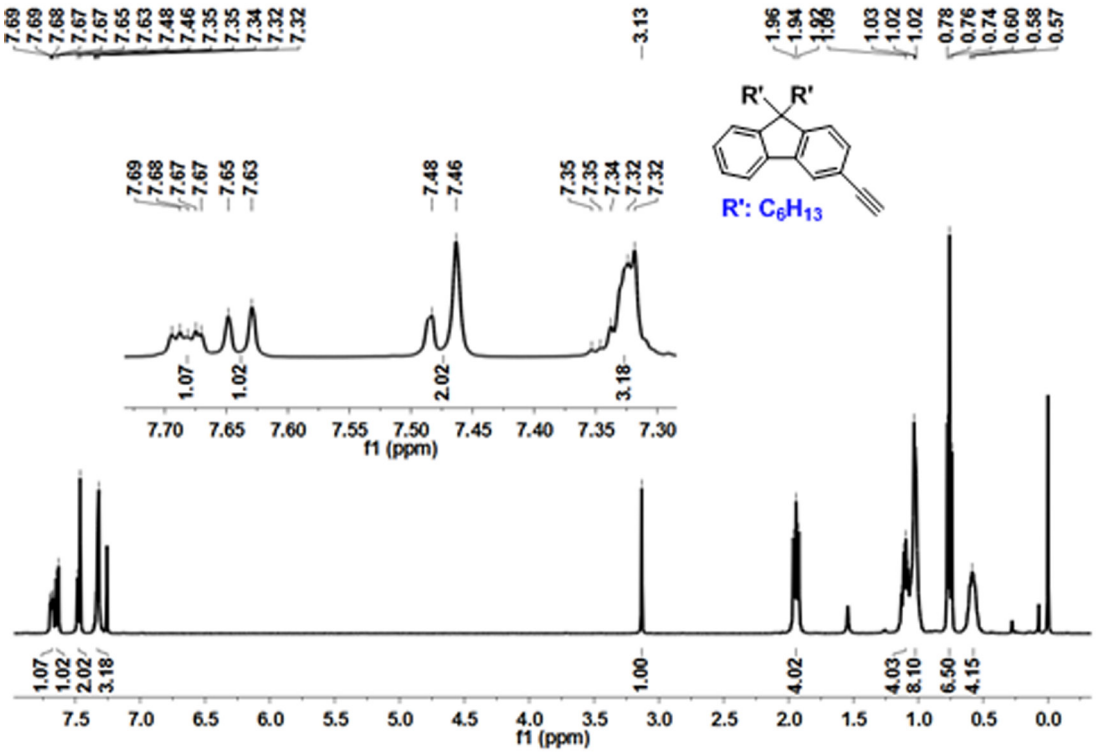


Fig. S4 ^{1}H-NMR of compound **4** in $CDCl_3$.

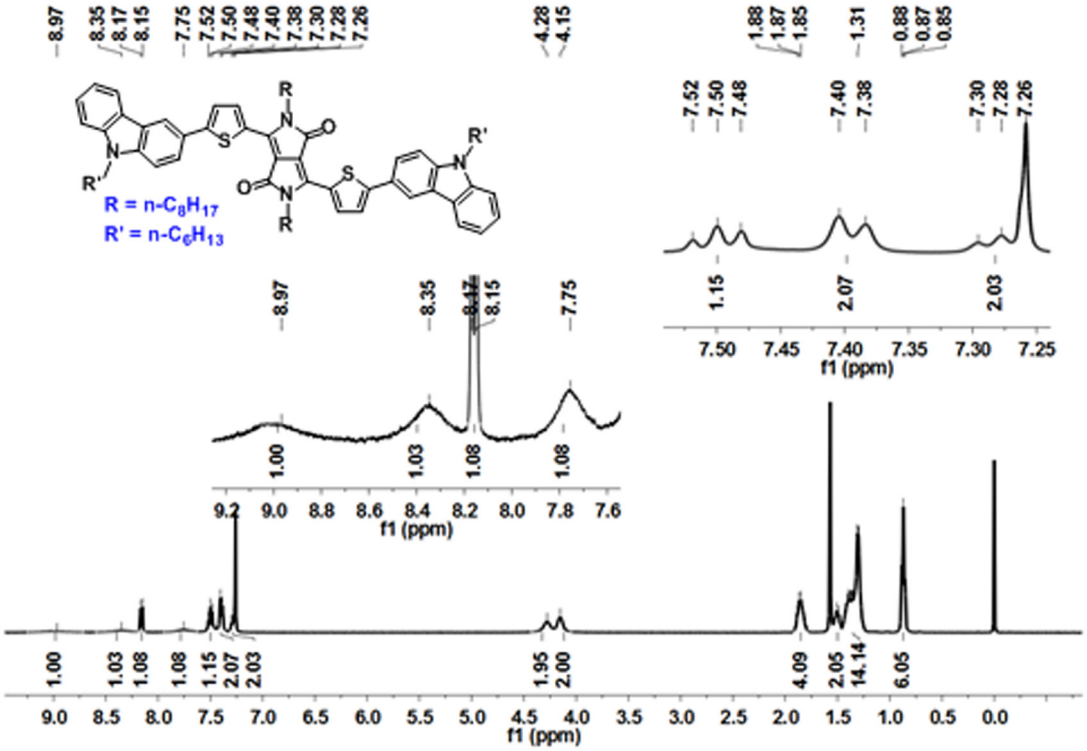


Fig. S5 ^{1}H-NMR of compound **M1** in $CDCl_3$.

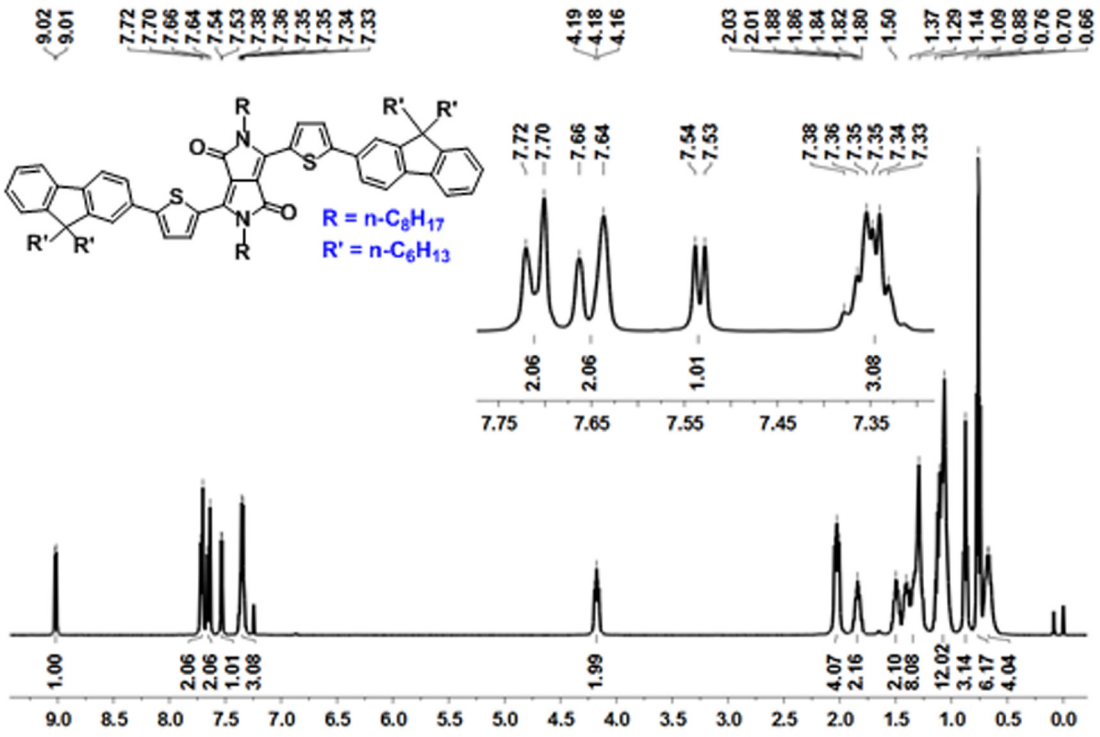


Fig. S6 ^{1}H-NMR of compound **M2** in $CDCl_3$.

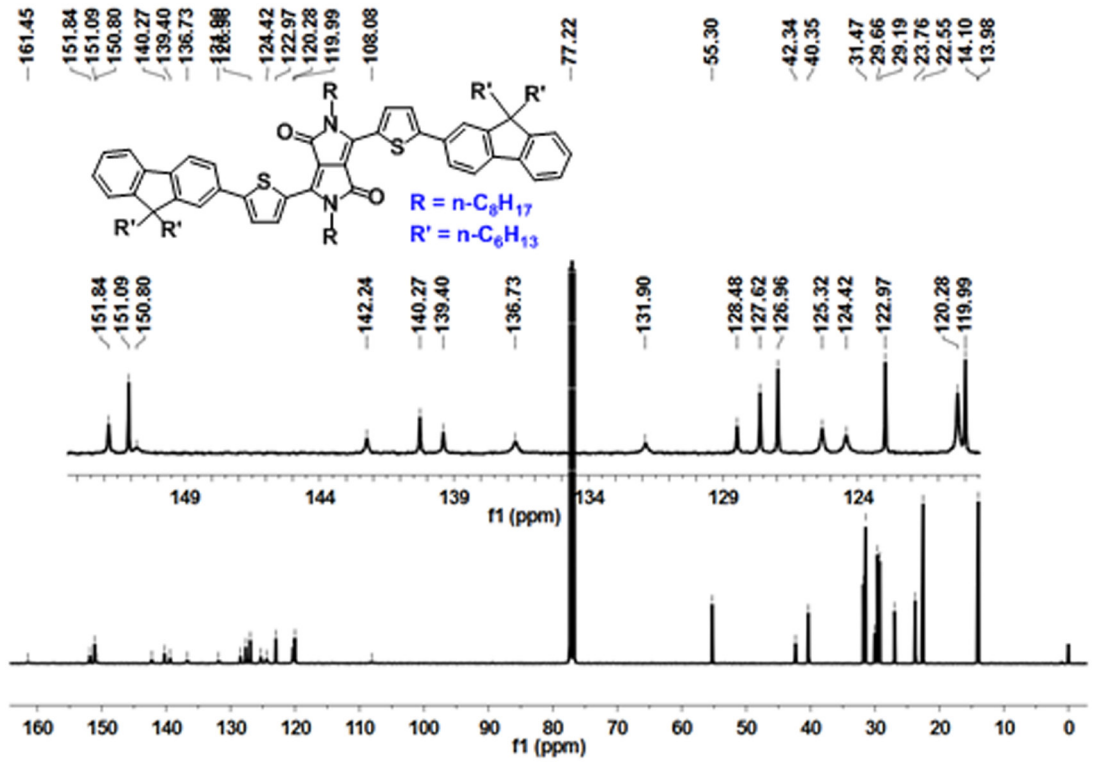


Fig. S7 ^{13}C-NMR of compound **M2** in $CDCl_3$.

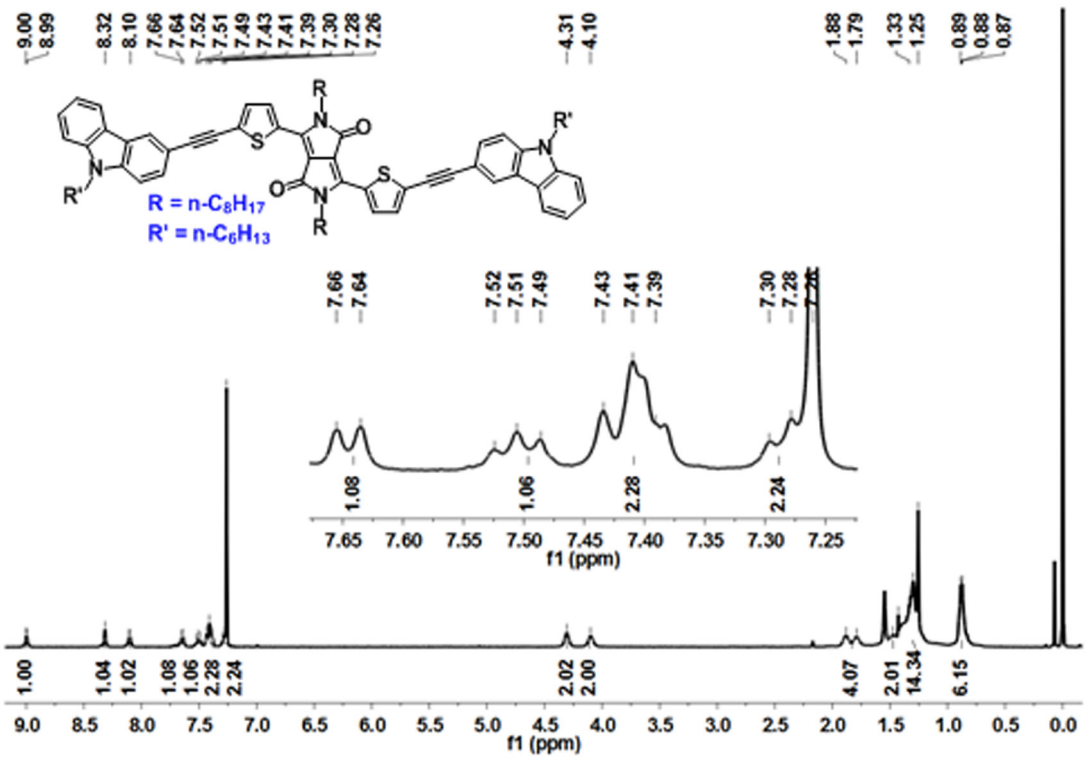


Fig. S8 ^{1}H-NMR of **M3** in $CDCl_3$.

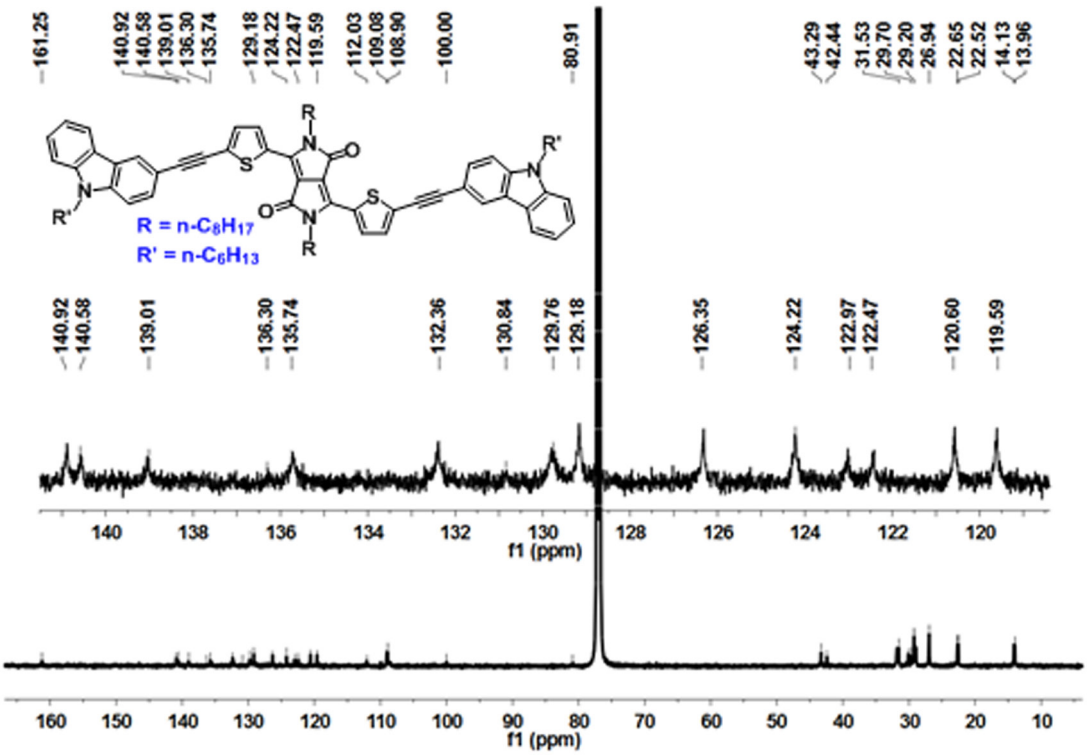


Fig. S9 ^{13}C-NMR of compound **M3** in $CDCl_3$.

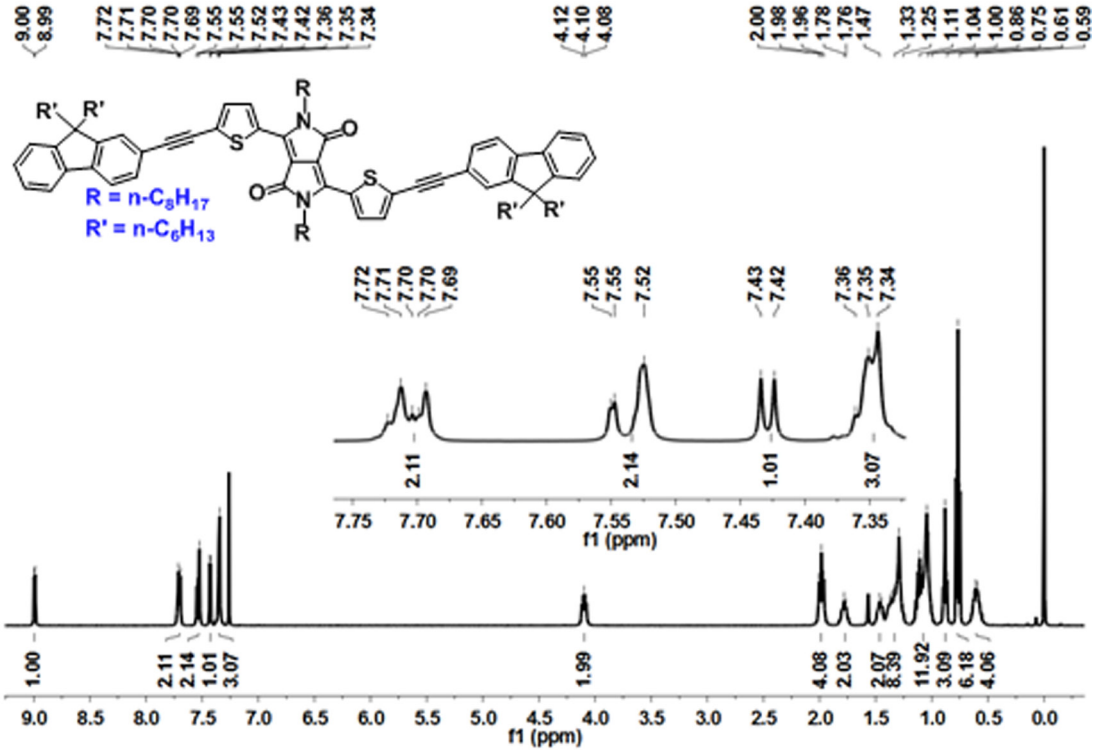


Fig. S10 ^{1}H-NMR of compound **M4** in $CDCl_3$.

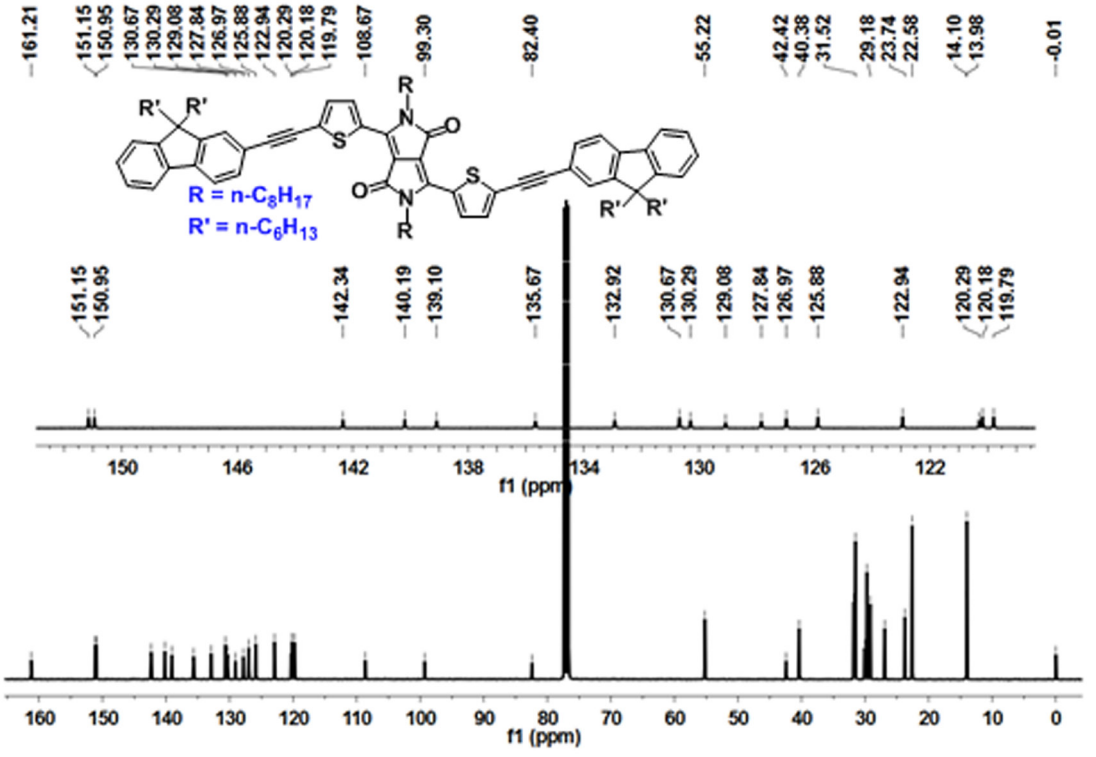


Fig. S11 ^{13}C-NMR of compound **M4** in $CDCl_3$.