

Supplementary information

Design and synthesis new ultra low band gap thiadiazolouinoxaline based polymers for near infrared organic photovoltaic application.

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Experimental section

Materials.

All starting reagents were obtained commercially as analytical reagent and used directly without any purification. Toluene and tetrahydrofuran (THF) were refluxed over sodium and benzophenone, and distilled prior to use. Column chromatography was carried out on silica gel (Qingdao Haiyang Chem. Co. LTD, 200-300mesh).

Characterization

¹H and ¹³C NMR spectra of the starting compounds and copolymers were recorded on the spectrometer “Bruker Avance-400” with a working frequency of 400.13 and 100.62 MHz, respectively. IR spectra were recorded by a FT-IR spectrometer “Perkin -Elmer 1720-X”. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography(GPC) analysis with polystyrene standard calibration (Waters high pressure GPC assembly model 1515 pump, refractive index detectors , solvent THF). TGA and DSC analysis was performed on “Per-kin-Elmer TGA-7” and “Perkin Elmer DSC 7” devices with heating rate of 20 deg/min. UV-Vis-NIR spectra of the polymers were recorded on a Perkin – Elmer Lambda 25 spectrometr. Cyclic voltammetry measurements were performed on a potentiostat-galvanostat AUTOLAB Type III equipped with standard three-electrode scheme in an acetonitrile solution of 0.1 mol/L tributylammonium perchlorate (n Bu₄NCIO₄) at a potential scan rate of 50 mV/s. Films of investigated polymers were deposited on a glass

surface coated with ITO and then dried and used as working electrode. Ag/Ag. and platinum were used as reference and counter electrodes, respectively.

Synthesis of the monomers and polymers

α -Ethylstearic acid (2): *n*-BuLi (156 ml, 0.39 mol, 2.5 M hexane solution) was added dropwise to a solution of diisopropylamine (42.7 g, 0.42 mol) and tetramethylethylenediamine (6.1g, 214 mmol) in 120 ml of THF at -50°C. During addition the temperature of the reaction mixture raised to -20°C. The mixture was stirred at that temperature for 40 h, cooled to -30°C, and then a solution of steric acid (50 g, 0.17 mmol) in 150 ml of THF was added. Reaction mixture was warmed to room temperature, stirred at that temperature for 1 h, then stirred at 50°C for 1 h, and cooled to -20°C. At this temperature ethyl iodide (32.9 g, 0.21 mol) was added, the mixture was warmed to 20°C, stirred for 3 h at this temperature, and heated at 50°C for 30 h. After cooling the reaction mixture was poured in a mixture of water (1000 ml), concentrated HCl (100 ml) and hexane (800 ml), organic phase was separated and washed with water (4×500 ml). To the hexane solution SiO₂ (20 g) was added, the mixture was stirred for 30 min, filtrated, and evaporated. The yield of title compound is 55 g (100%). ¹H NMR (300 MHz, CDCl₃, δ ppm): 0.92 (m, 6H), 1.30 (m, 28H), 1.57 (m, 4H), 2.33 (m, 1H) (Figure S1).

α -Ethylstearic acid carboxamide (3). Suspension of carbonyldiimidazole (34.2 g, 211 mmol) in THF (100 ml) was added to a solution of α -ethylstearic acid (**2**) (55 g, 176 mmol) in THF (150 ml) with vigorous stirring, then the mixture was stirred at 50°C for 1 h, and cooled to 25°C. This solution was added to a mixture of aqueous NH₃ solution (400 ml) and THF (200 ml) and -5°C, and then stirred at room temperature overnight. Precipitate was filtrated, dried, dissolved in refluxing mixture of CH₂Cl₂ (900 ml) and isopropanol (50 ml), and cooled. Precipitate was filtered and dried. Yield of title compound is 38.3 g (70%). ¹H NMR (300 MHz, CDCl₃, δ ppm): 0.92 (m, 6H), 1.30 (m, 28H), 1.61 (m, 4H), 2.38 (m, 1H) (Figure S2).

α -Ethylstearic acid thiocarboxamide (4). A mixture of α -ethylstearic acid (**3**) (38.3 g, 123 mmol), Lawesson's reagent (54.7 g, 135 mmol) and 250 ml THF was stirred at 42°C for 40 h under argon. Reaction mixture was evaporated, residue was dissolved in CHCl₃ (200 ml), organic phase was washed with water (3×300 ml), dried with Na₂SO₄, filtrated and evaporated in vacuum. The residue was purified on SiO₂ with CHCl₃ as an eluent. After evaporation the title compound **3** was obtained with the yield of 25.1 g (62%). ¹H NMR (300

MHz, CDCl₃, δ ppm): 0.91 (m, 6H), 1.26 (m, 28H), 1.67 (m, 4H), 2.42 (m, 1H), 6.97 (br.s, 1H), 7.68 (br.s, 1H) (Figure S3).

2-(1-Ethylheptadecyl)-1,3-thiazole (5). Bromoacetyl aldehyde diethylacetal (20.3 g, 103 mmol) was added to a solution of stearic acid thiocarboxamide (**4**) (25.0 g, 76 mmol) in dimethoxyethane (200 ml), then a catalytic amount of concentrated hydrochloric acid was added, and the reaction mixture was heated at 85°C for 5 h under inert atmosphere (the reaction was monitored by TLC, eluent – CHCl₃). Reaction mixture was evaporated, then hexane (250 ml) and concentrated HCl (50 ml) were added, the solids precipitated were collected by filtration. The solids obtained were re-dissolved in THF and NEt₃ (10.0 g, 100 mmol) was added; after stirring for 20 min twice the volume of hexane was added, and the mixture was passed through a SiO₂ pad (1 cm), the filtrate was evaporated. The residue was purified by column chromatography on SiO₂ using a mixture CH₂Cl₂:hexane=1:1 as eluent. Title compound was obtained as light oil with the yield of 20 g (75%). ¹H NMR (400 MHz, CDCl₃, δ ppm): 0.88 (m, 6H), 1.26 (m, 28H), 1.75 (m, 4H), 3.03 (m, 1H), 7.21 (d, $J=3.40$ Hz, 1H), 7.70 (d, $J=3.40$ Hz, 1H) (Figure S4).

5-Bromo-2-(1-ethylheptadecyl)-1,3-thiazole (6). *t*-BuLi (50 ml, 79 mmol, 1.6 M pentane solution) was added dropwise to a solution of 2-(1-ethylheptadecyl)-1,3-thiazole (**5**) (20.0 g, 57 mmol) in 250 ml THF at -85°C. After the addition was completed the reaction mixture was mechanically stirred for additional 2.5 h at that temperature. Then a solution of CBr₄ (24.6 g, 74 mmol) in 150 ml THF was added dropwise to the reaction mixture at -85°C. The black reaction mixture was stirred at -60°C for 30 min and warmed to room temperature. Reaction mixture was filtrated through SiO₂ (300 g), with additional elution with CHCl₃, and solvents were evaporated. The residue was purified by column chromatography using CHCl₃-hexane= 80:20 mixture as an eluent. After evaporation the title compound **6** was obtained as dark oil with the yield of 20.0 g (82%). ¹H NMR (400 MHz, CDCl₃, δ ppm): 0.89 (t, $J=7.02$ Hz, 6H), 1.27 (m, 28H), 1.76 (m, 4H), 2.94 (m, 1H), 7.56 (s, 1H) (Figure S5).

4,4'-Dibromo-2,2'-bis(1-ethylheptadecyl)-5,5'-bithiazole-1,3 (7). *n*-BuLi (22 ml, 55 mmol, 2.5 M hexane solution) was added dropwise to a solution of diisopropylamine (5.6 g, 56 mmol) in 100 ml THF at -50°C, then the reaction mixture was stirred at -20°C for 40 min, and cooled to -80°C. To this LDA solution a solution of 5-bromo-2-(1-ethylheptadecyl)-1,3-thiazole (**6**) (19.6 g, 46 mmol) in 120 ml of THF was added dropwise. After the addition was

completed, the reaction mixture was stirred at -75°C for 1.5 h, cooled to -85°C , and then CuCl_2 (8 g, 56 mmol) was added in one portion. The resulting dark solution was stirred for 30 min at -60°C and warmed to RT. The reaction mixture was diluted with twice volume of hexane, evaporated with SiO_2 (350 g), and eluted with hexane- $\text{CHCl}_3 = 90:10$. After evaporation the residue was purified on SiO_2 column with a mixture hexane- $\text{CHCl}_3 = 90:10$ as an eluent. Solvents were removed in vacuum and product **7** was obtained as yellow oil, which easily crystallizes on standing. The yield is 17.7 g (91 %). $^1\text{H NMR}$ (300 MHz, CDCl_3 , δ ppm): 0.91 (dt, $J=17.84$, 7.14 Hz, 12H), 1.26 (m, 56H), 1.78 (m, 8H), 2.96 (dq, $J=7.18$, 6.96 Hz, 2H) (Figure S6). HRMS, calculated for $\text{C}_{44}\text{H}_{78}\text{Br}_2\text{N}_2\text{S}_2^+\text{H}$ 857.4046, 859.4029, 861.4007. Found: 857.4031, 859.4016, 861.4014.

2,7-Di(1-ethylheptadecyl)[1,3]thiazolo[4,5-g][1,3]benzothiazol-4,5-dione (8). *t*-BuLi (85 ml, 136 mmol, 1.6 M pentane solution) was added dropwise to the solution of 4,4'-dibromo-2,2'-bis(1-ethylheptadecyl)-5,5'-bithiazole-1,3 (**7**) in 200 ml THF at -85°C , the reaction mixture was stirred at this temperature for 2 h, and then solution of diethyloxalate (11 g, 76 mmol) in 35 ml hexane was added in one portion. The dark reaction solution was stirred for 30 min at -60°C and warmed to 25°C . The reaction mixture was poured into NaH_2PO_4 solution (20 g, 170 mmol) in H_2O (200 ml) and stirred for 20 min. Then the mixture was acidified by slow addition of 3M HCl until pH of 3-4. Then hexane (200 ml) and Et_2O (60 ml) were added. Organic phase was separated and washed with water (4×200 ml). Organic solvents were evaporated in vacuum and residue was purified on SiO_2 using a gradient mixture of hexane/ $\text{CH}_2\text{Cl}_2 = 100:0 - 80:20$. Solution of diketone **8** was evaporated and the residue was refluxed with methanol and cooled. The pure title compound **8** was obtained as dark-red powder with the yield of 5.6 g (37%). $^1\text{H NMR}$ (300 MHz, CDCl_3 , δ ppm): 0.91 (dt, $J=17.18$, 7.08 Hz, 12H), 1.25 (m, 56H), 1.81 (m, 8H), 3.09 (m, 2H) (Figure S7). HRMS, calculated for $\text{C}_{46}\text{H}_{78}\text{N}_2\text{O}_2\text{S}_2^+\text{H}$ 755.5577. Found: 755.5572.

2-(Trimethylstannyl)-4-dodecylthiophene (11) [1] LDA solution (prepared from *n*-BuLi (50 ml, 80 mmol, 1.6 M hexane solution), diisopropylamine (11.21 ml, 80 mmol) in 100 ml THF) was added dropwise to a solution of 3-dodecylthiophene (16.156 g, 64 mmol) at -45°C . After the addition was completed, the mixture was warmed to 0°C , stirred for 40 min at that temperature, then cooled to -50°C , and a solution of Me_3SnCl in hexane (80 ml, 80 mmol, 1M) was added dropwise to the reaction mixture. After warming to room temperature reaction mixture was stirred for 3 h, then water (400 ml) was added. Organic phase was

separated, water layer was extracted with hexane. Organic phases were combined and washed with water, dried with Na₂SO₄, filtrated, and evaporated. Product was used without further purification. ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.25 (s, 1H), 7.06 (s, 1H), 2.7 (t, 2H), 1.67 (m, 2H), 1.50-1.25 (m, 18H), 0.94 (t, 3H), 0.41 (m, 9H). ¹³C NMR (100 MHz, CDCl₃, δ ppm): 144.63, 137.24, 125.68, 119.77, 31.98, 30.80, 30.62, 30.33, 30.03, 29.73-29.41 (br), 22.75, 14.18 (Figure S8).

4,7-Dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole (12)[2] Trifluoro methane sulfonic acid (7.5mL) and HNO₃ (8 mL) were added dropwise to concentrated H₂SO₄ (10 mL) at 0 °C. Compound 1 (2.00 g, 6.85 mmol) was added to the acid mixture at 0 °C. The mixture was kept at room temperature for 4 h before being poured into ice-water (100 mL) and then extracted with CH₂Cl₂. The organic layer was washed with water and brine, dried with MgSO₄, filtered, concentrated via rotary evaporation and purified by column chromatography on silica gel with ethyl acetate:petroleum ether (1:10, v/v) as eluent to give pure compound 12 as a pale yellow solid (1.58 g, 40%).

4,7-Bis(4-(dodecylthiophen-2-yl)-5,6-dinitrobenzo[*c*][1,2,5] thiadiazole (13) [3] Pd(PPh₃)₄ (1.5g, 0.96 mmol) was added to a solution of 2-trimethyltin-4-dodecylthiophen(11) (35.165 g, 84.68 μmol) and 4,7-dibromo-5,6-dinitrobenzothiadiazole (9.88 g, 25.73 μmol) in anhydrous THF (600mL). The reaction mixture was then heated at 80 °C for 20 h. After cooling to room temperature, the solvent was evaporated and the crude product was washed with hexane and dried to give pure compound 4 as an orange solid (13.43 g, 72%). NMR ¹H (400 MHz, CDCl₃, δ ppm): 7.35 (s, 4H), 2.69 (t, 4H), 1.68 (m, 4H), 1.50-1.20 (m, 36H), 0.91 (t, 6H). NMR ¹³C (100 MHz, CDCl₃, δ ppm.): 152.19, 144.41, 141.65, 132.17, 129.20, 126.41, 121.39, 31.94, 30.35, 30.26, 29.68, 29.66, 29.60, 29.45, 29.37, 29.24, 22.71, 14.13 (Figure S9).

4,7-Bis(4-(2-ethylhexyl)thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole-5,6-diamine(14)[3] Iron dust (12.41 g, 222 μmol) was added to a solution of compound 13 (13.43 g, 18.47 μmol) in acetic acid (350 mL). The mixture was heated at 75 °C for 5 h before being cooled to room temperature, poured into the water, and extracted with ether. The organic layer was washed with water and brine, dried with MgSO₄, filtered, concentrated via rotary evaporation NMR ¹H (400 MHz, CDCl₃, δ ppm.): 7.19 (s, 2H), 7.12 (s, 2H), 2.69 (t, 4H), 1.68 (m, 4H), 1.50-1.20 (m, 36H), 0.91 (t, 6H). NMR ¹³C (100 MHz, CDCl₃, δ ppm): 152.19, 144.41,

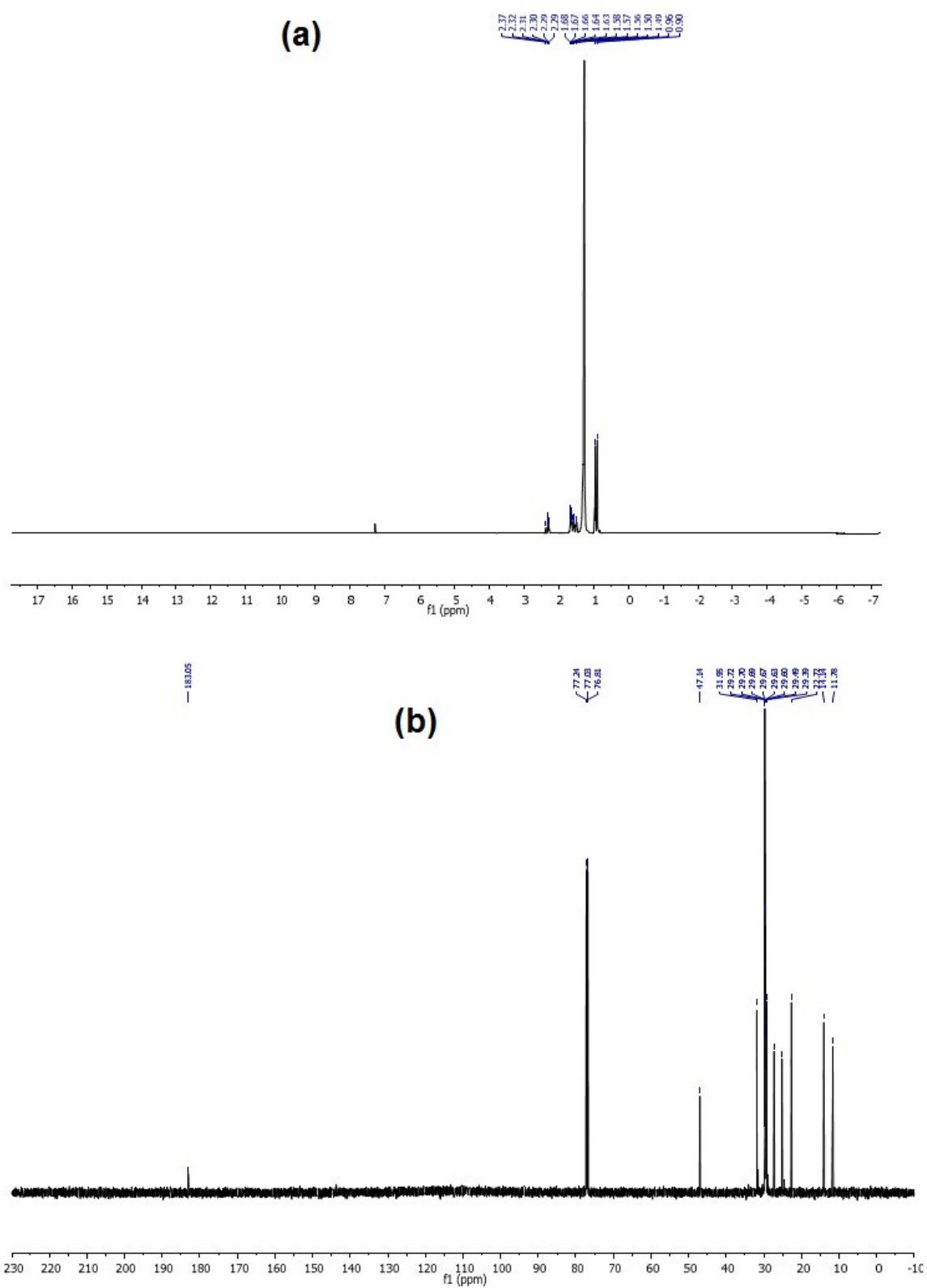
141.65, 132.17, 129.20, 126.41, 121.39, 32.00, 30.63, 30.48, 29.77, 29.74, 29.58, 29.56, 29.44, 22.77, 14.21 (Figure S10).

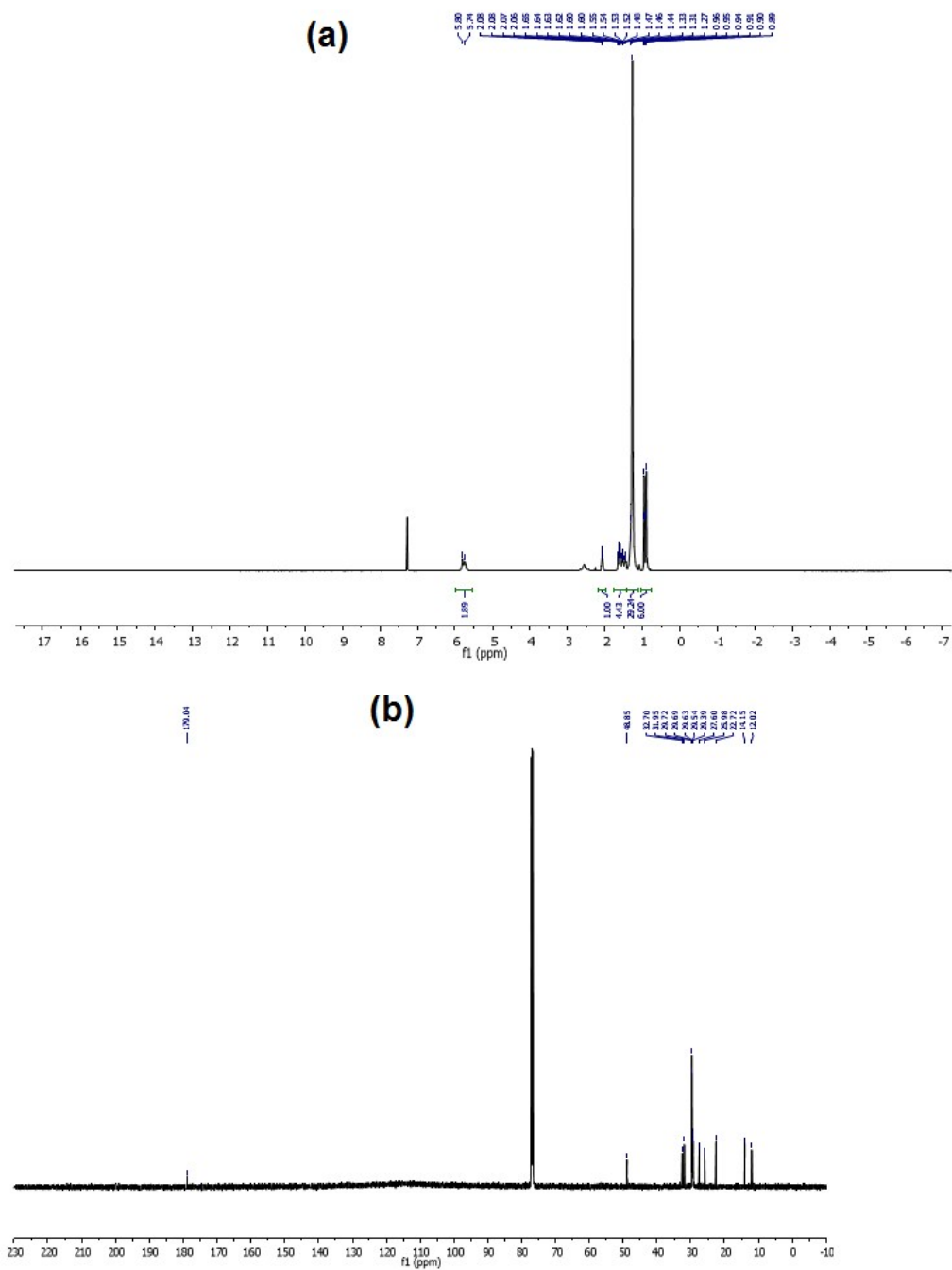
8,12-Bis(4,5-didodecythiophen-2-yl)-2,5-di(nonadecan-3-yl)[1,2,5] thiadiazolo [3,4-i] bis [1,3] thiazolo[4,5-a:5',4'-c]phenazine (15). A solution of diamine **14** (214 mg, 0.321 mmol), diketone **8** (242 mg, 0.321 mmol) in a mixture of AcOH (15 ml) and dioxane (15 ml) was heated at 65°C overnight. After cooling to RT, water (100 ml) was added, precipitate was collected by filtration, washed with water and CH₃OH, dried in vacuum and purified on SiO₂ column (hexane-CHCl₃ = 1:1). The yield is 364 mg (82%). ¹H NMR (400 MHz, CDCl₃, δ ppm): 9.26 (s, 2H), 7.40 (s, 2H), 3.35 (m, 2H), 2.85 (m, 4H), 2.2-1.75 (m, 12H), 1.6-1.25 (m, 98H), 0.9 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, δ ppm): 176.44, 151.34, 146.76, 143.32, 138.09, 137.21, 136.00, 135.65, 130.69, 127.67, 121.15, 46.74, 35.66, 31.94, 31.92, 30.78, 29.76-29.56, 29.38, 29.36, 29.06, 27.40, 22.69, 14.12, 11.97 (Figure S11).

4,7-dibromo-2,1,3-benzothiadiazole-5,6-diamine (16) [4] To a stirred solution of compound **3** (1 g, 2.6 mmol) in glacial acetic acid (20 ml), 1.75 g, of fine iron powder (31.25 mmol) was added portion wise at 0°C. The reaction mixture was stirred at ambient temperature for 12 h. Then the reactant was poured into ice cold water and the precipitate was filtered off. The obtained product was washed with water, followed by methanol to get yellow solid. Yield: 65 %. ¹H NMR (CDCl₃, 400 MHz), δ(ppm):5.49 (br, s, 4H).

References

1. L. Biniek, S. Fall, Ch. L. Chochos, D. V. Anokhin, D. A. Ivanov, N. Leclerc, †P. Leveque, and T. Heiser/ *Macromolecules* 2010, 43, 9779–9786
2. E. Wang, L. Hou, Z. Wang, S. Hellstrom, W. Mammo, F. Zhang, O. Inganäs, and M. R. Andersson /*Org.lett.*2010.12.4470-4473
- 3 (a) C. An, M. Li, T. Marszalek, X. Guo, W. Pisula and M. Baumgarten/ *J. Mater. Chem. C*, 2015,**3**, 3876-3881; b) C. An, R. Puniredd, T. Stelzzing, Y. Zhao, W. Pisula, and M. Baumgarten /*Macromolecules*, 2014,**47**,979-986
4. G. Zhang, Y. Fu, Q. Zhang, Z. Xie / *Polymer*,2010,**51**,2313-2319





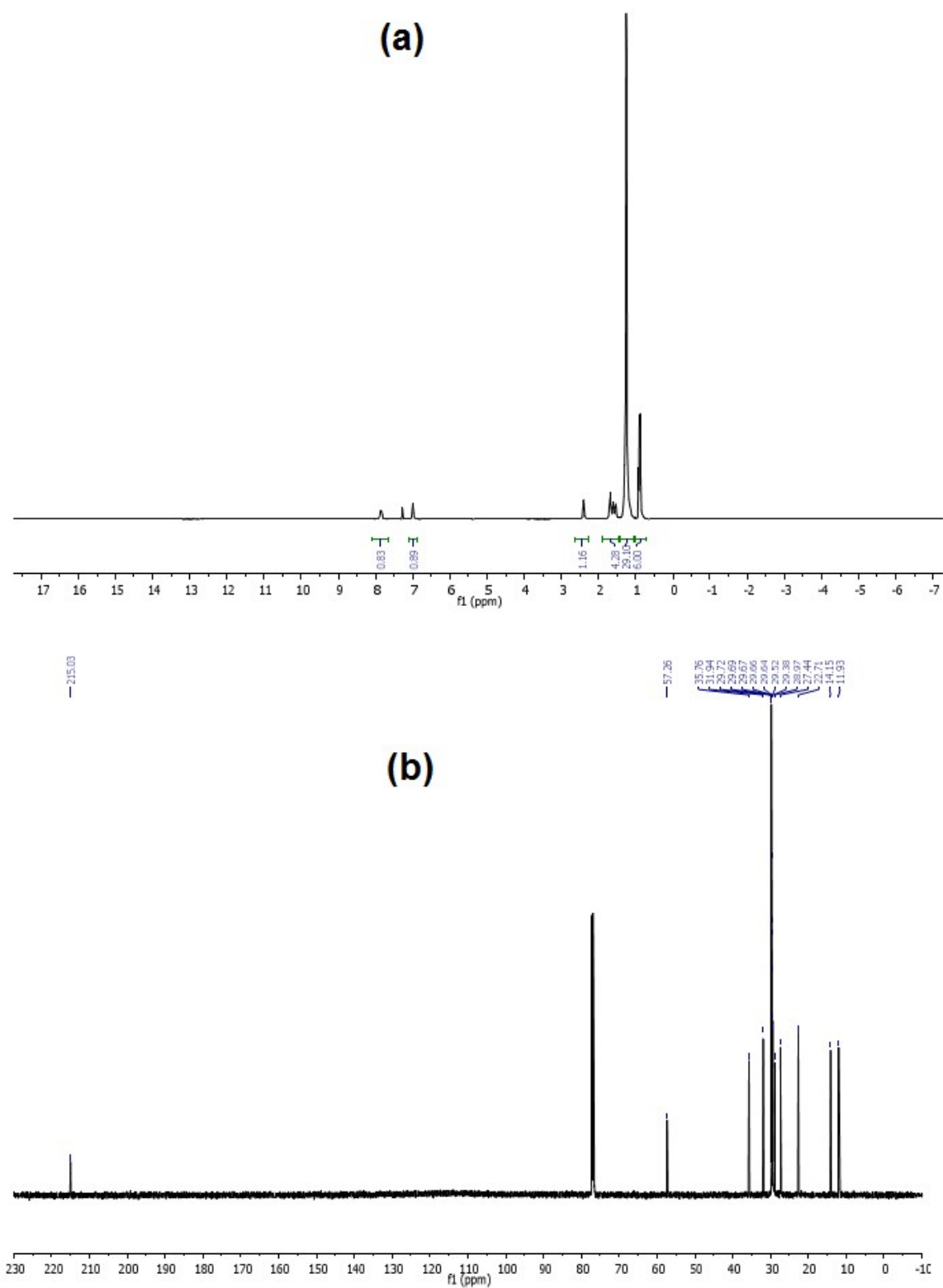


Fig. S3 ^1H (a) and ^{13}C (b) NMR spectra for α -Ethylstearic acid thiocarboxamide (4).

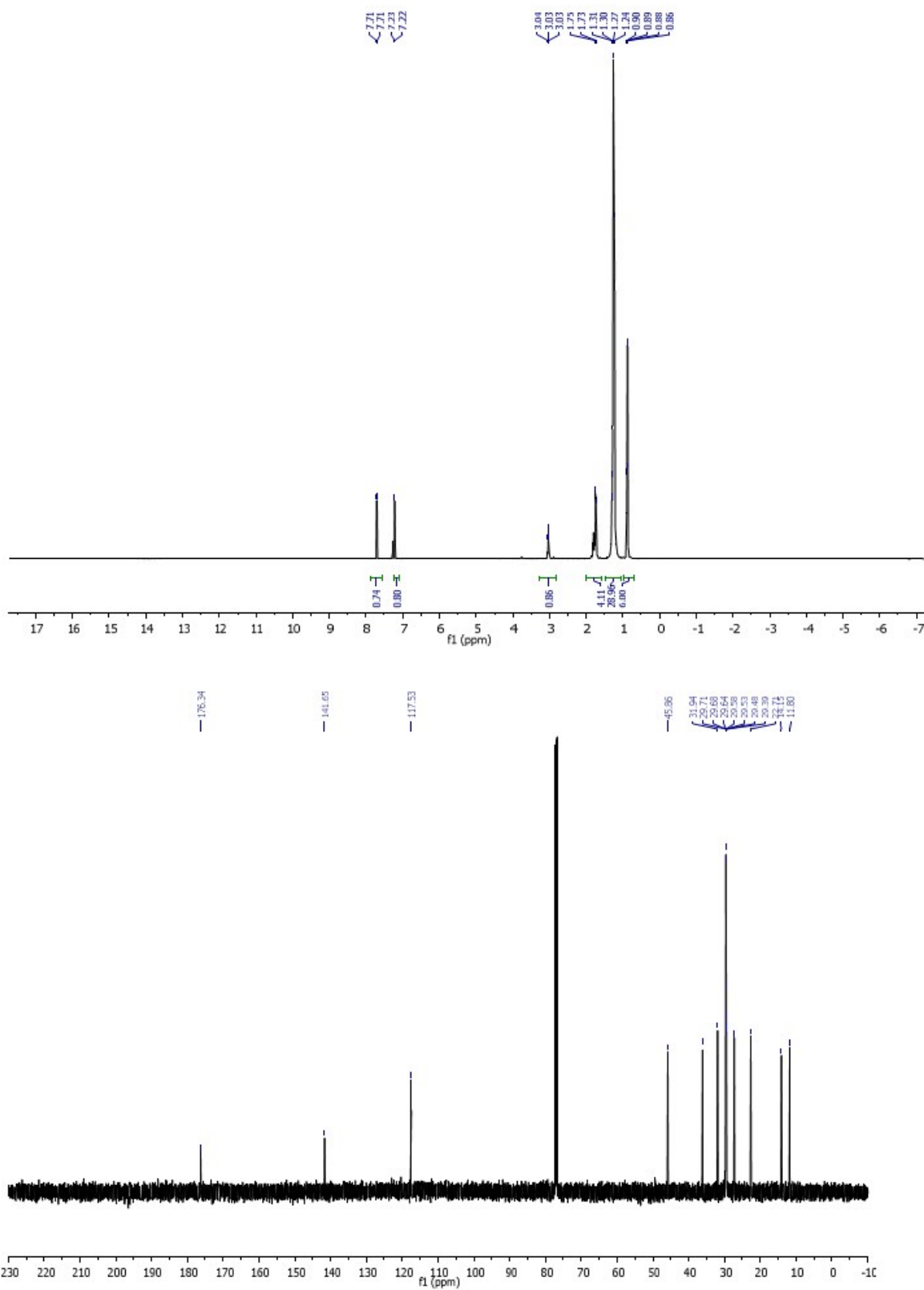


Figure S4 ^1H (a) and ^{13}C (b) NMR spectra for **2.4.5. 2-(1-Ethylheptadecyl)-1,3-thiazole (5)**.

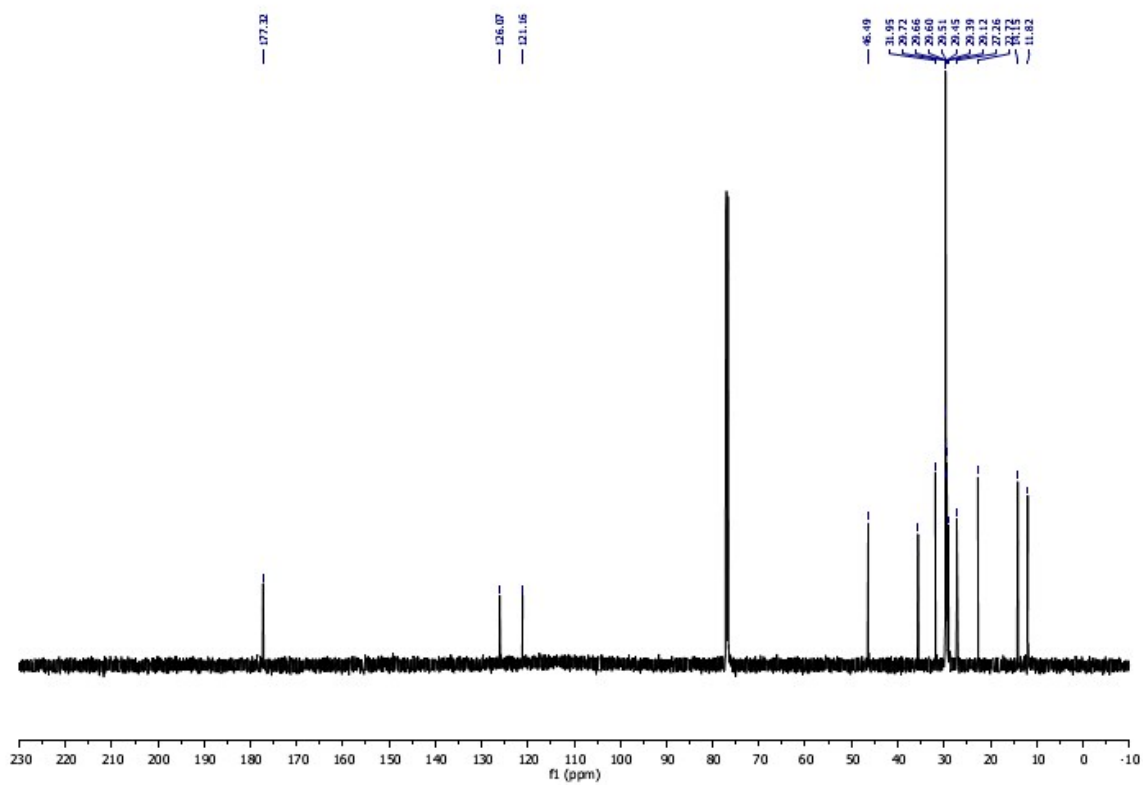
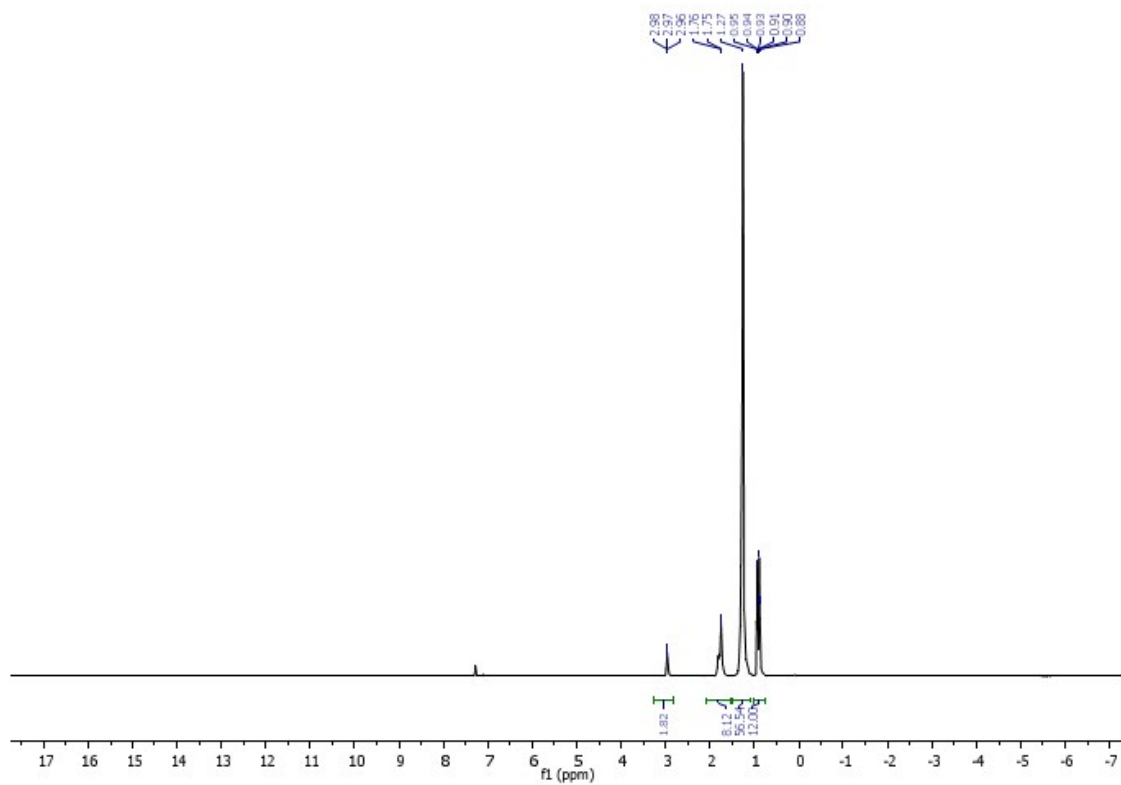


Figure S5 ¹H (a) and ¹³C (b) NMR spectra for 4,4'-Dibromo-2,2'-bis(1-ethylheptadecyl)-5,5'-bithiazole-1,3 (7).

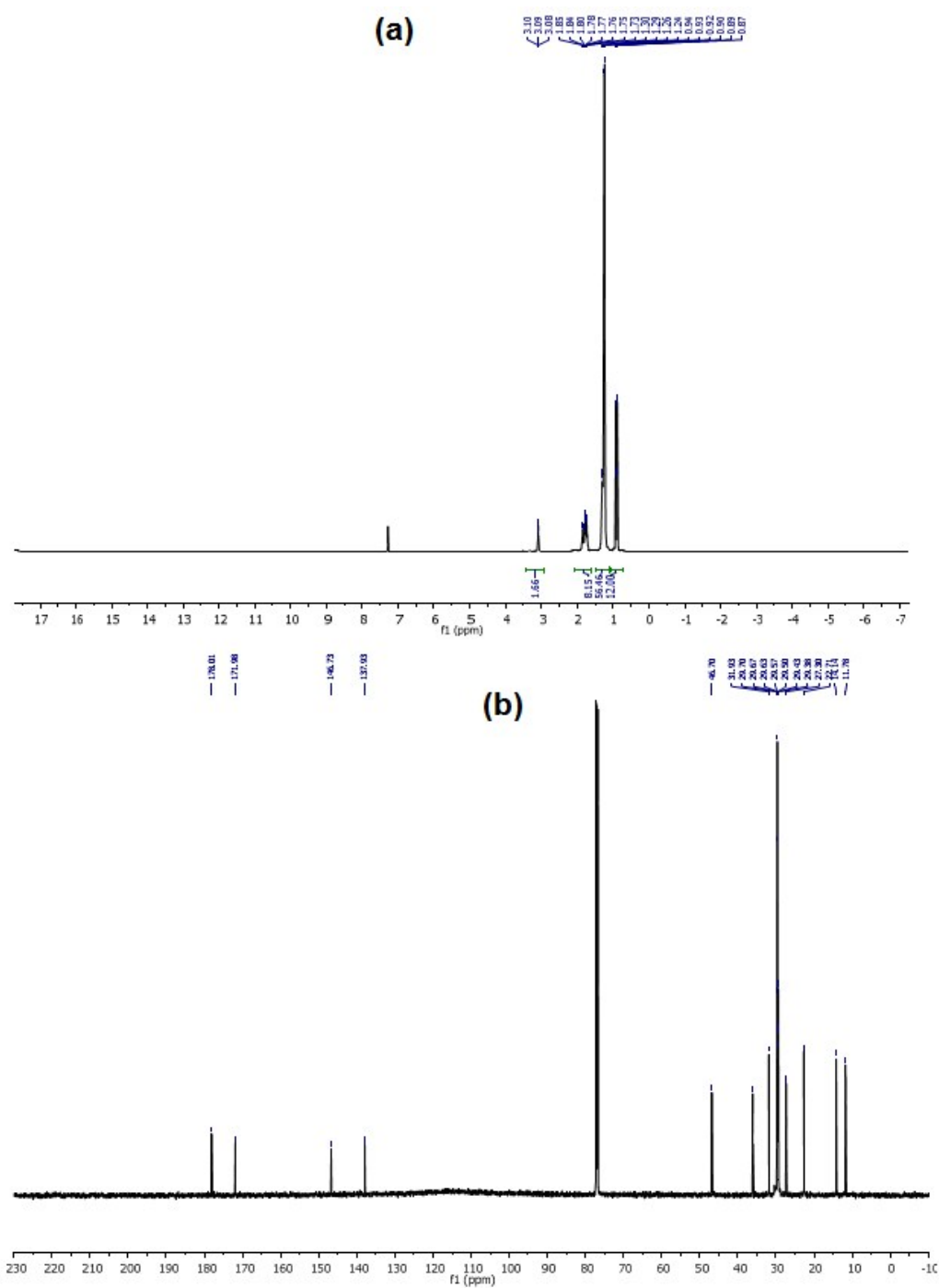
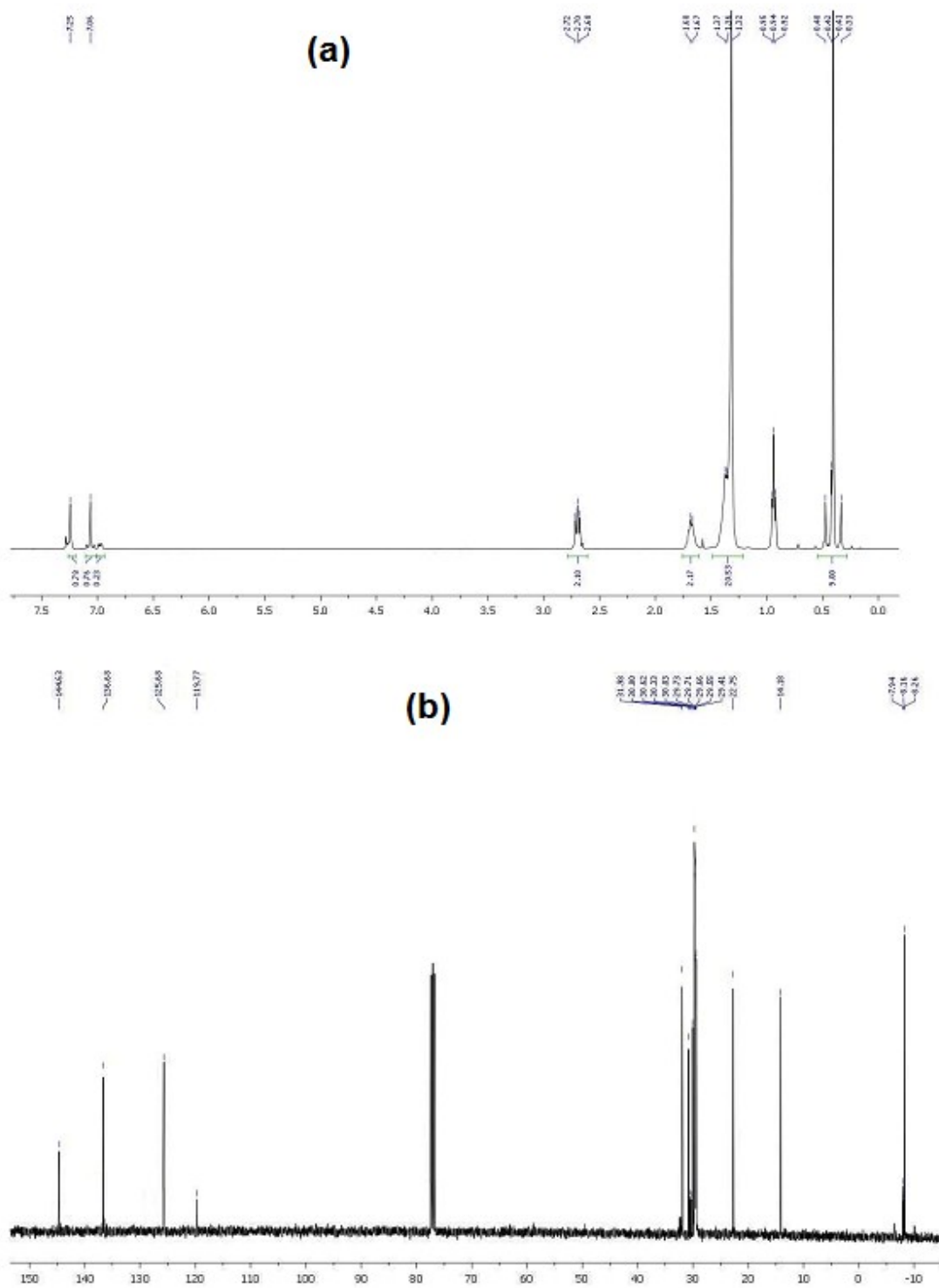


Figure S6 ¹H (a) and ¹³C (b) NMR spectra for 2,7-Di(1-ethylheptadecyl)[1,3]thiazolo[4,5-g][1,3]benzothiazol-4,5-dione (8)



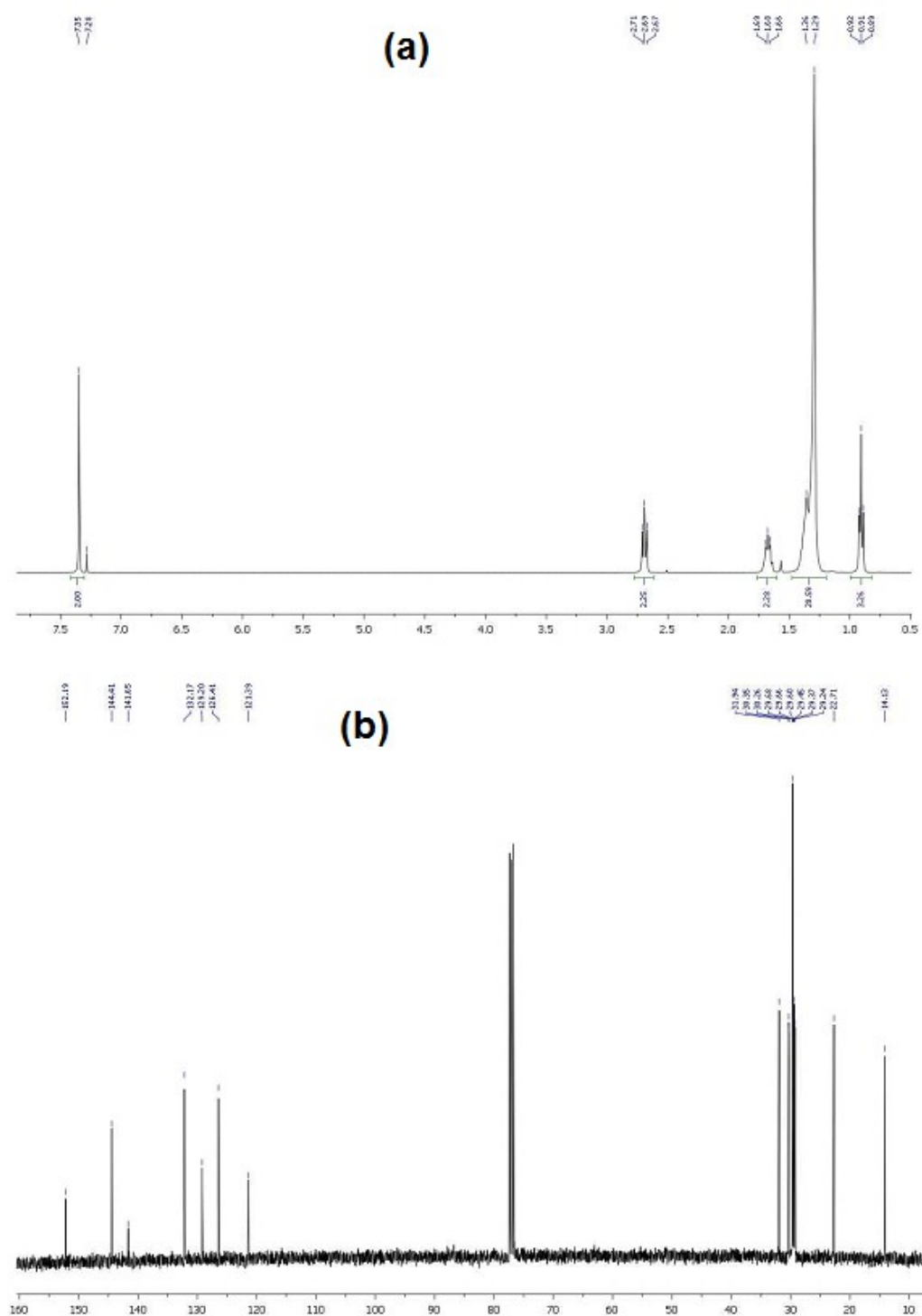


Figure S8 ^1H (a) and ^{13}C (b) NMR spectra for *4,7-Bis(4-(dodecylthiophen-2-yl)-5,6-dinitrobenzo[c][1,2,5]thiadiazole (13)*

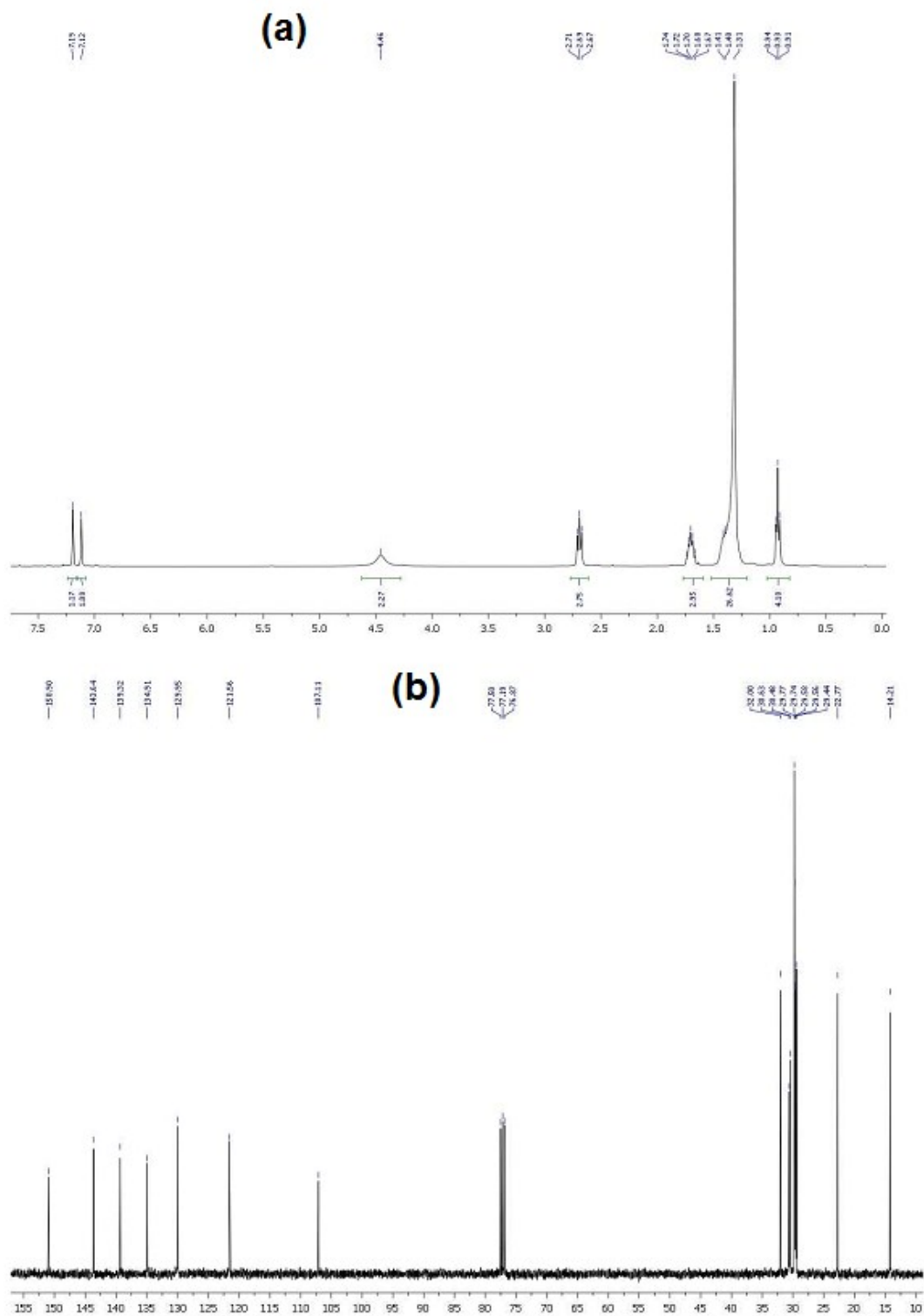


Figure S9 ^1H (a) and ^{13}C (b) NMR spectra for 4,7-Bis(4-(2-ethylhexyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole-5,6-diamine (14)

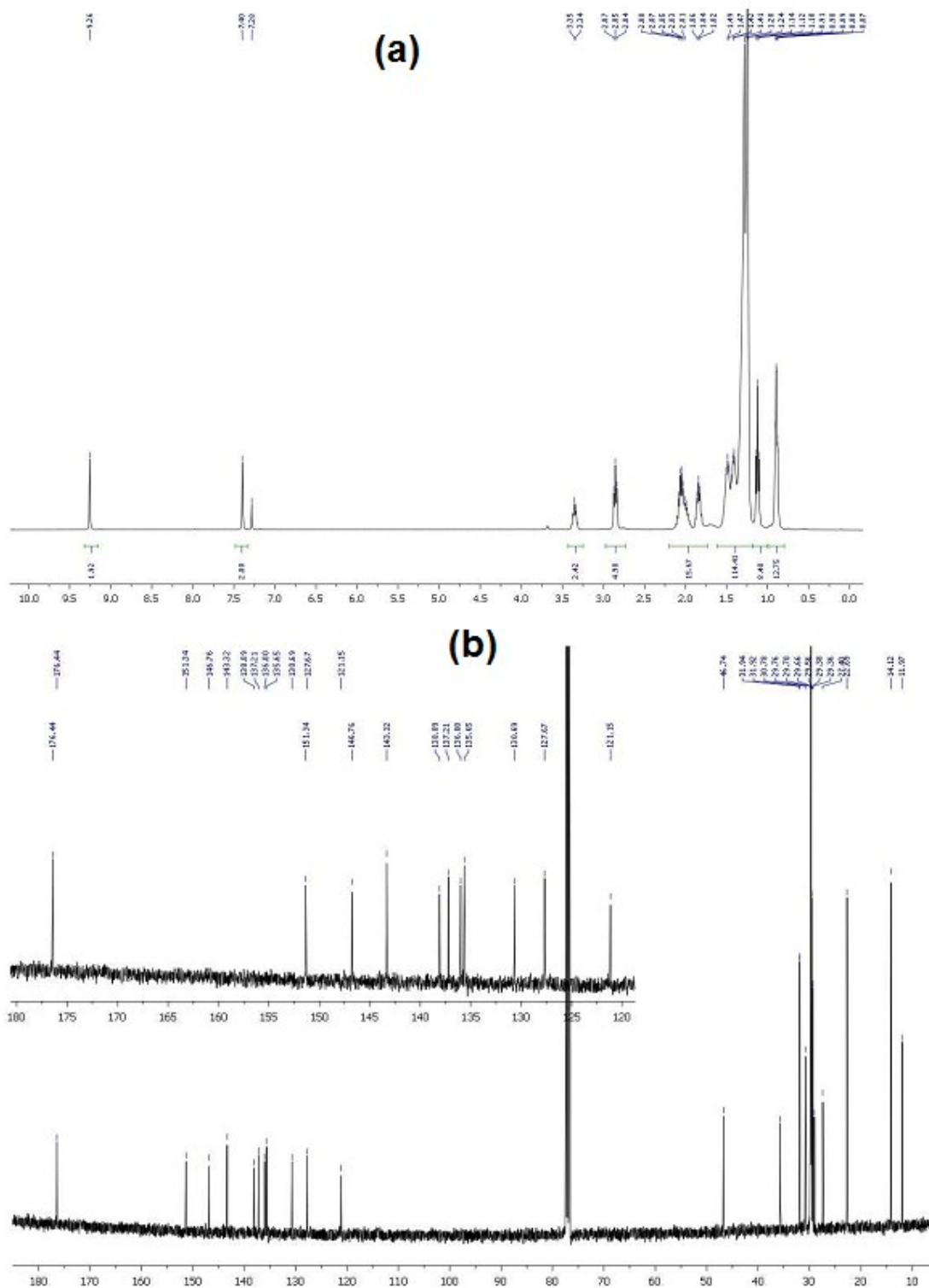


Figure S10 ¹H (a) and ¹³C (b) NMR spectra for 8,12-Bis(4,5-didodecythiophen-2-yl)-2,5-di(nonadecan-3-yl)[1,2,5]thiadiazolo[3,4-i]bis [1,3] thiazolo[4,5-a:5',4'-c]phenazine (15).

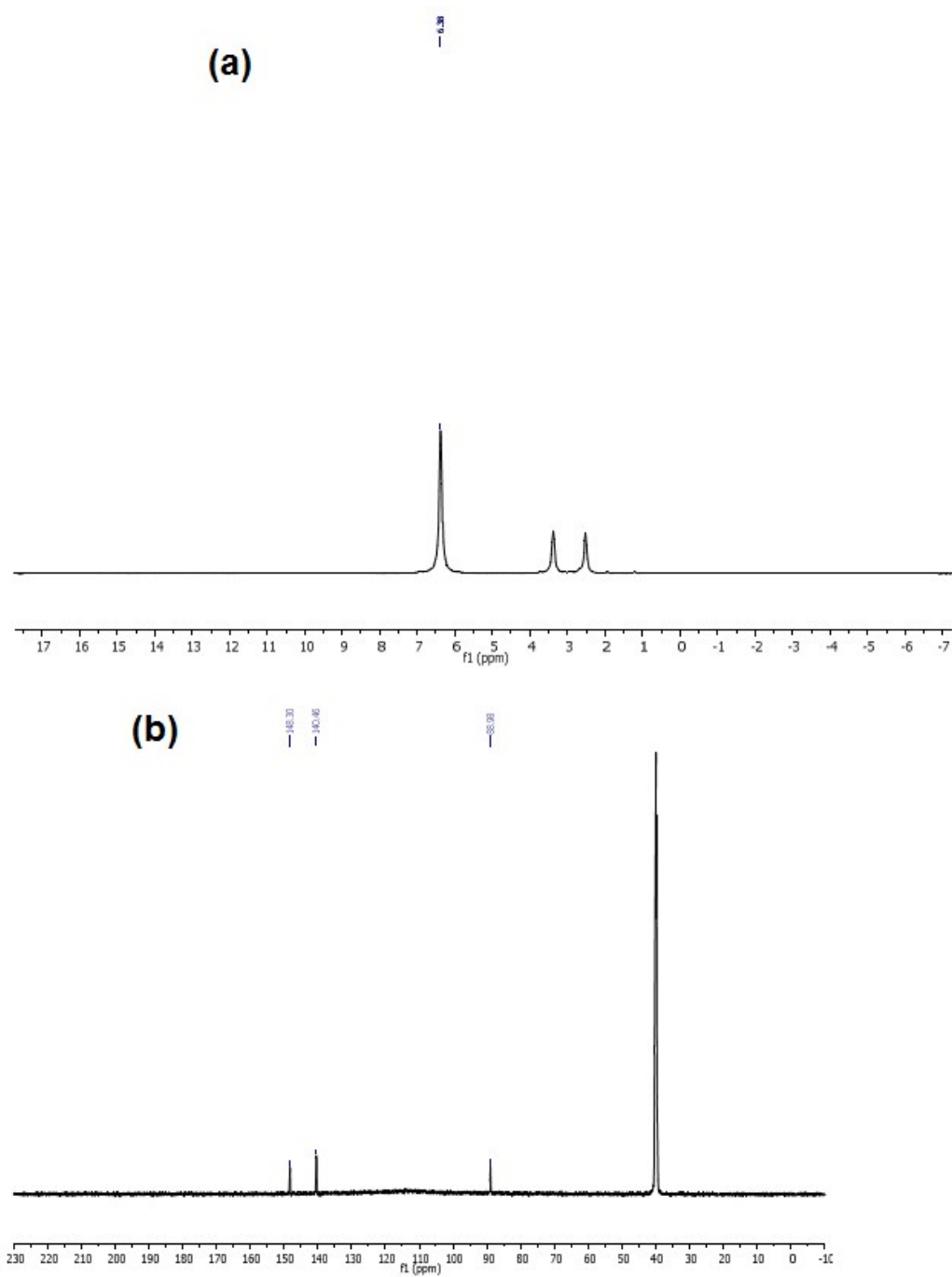


Figure S11 ^1H (a) and ^{13}C (b) NMR spectra for 4,7-dibromo-2,1,3-benzothiadiazole-5,6-diamine (16)

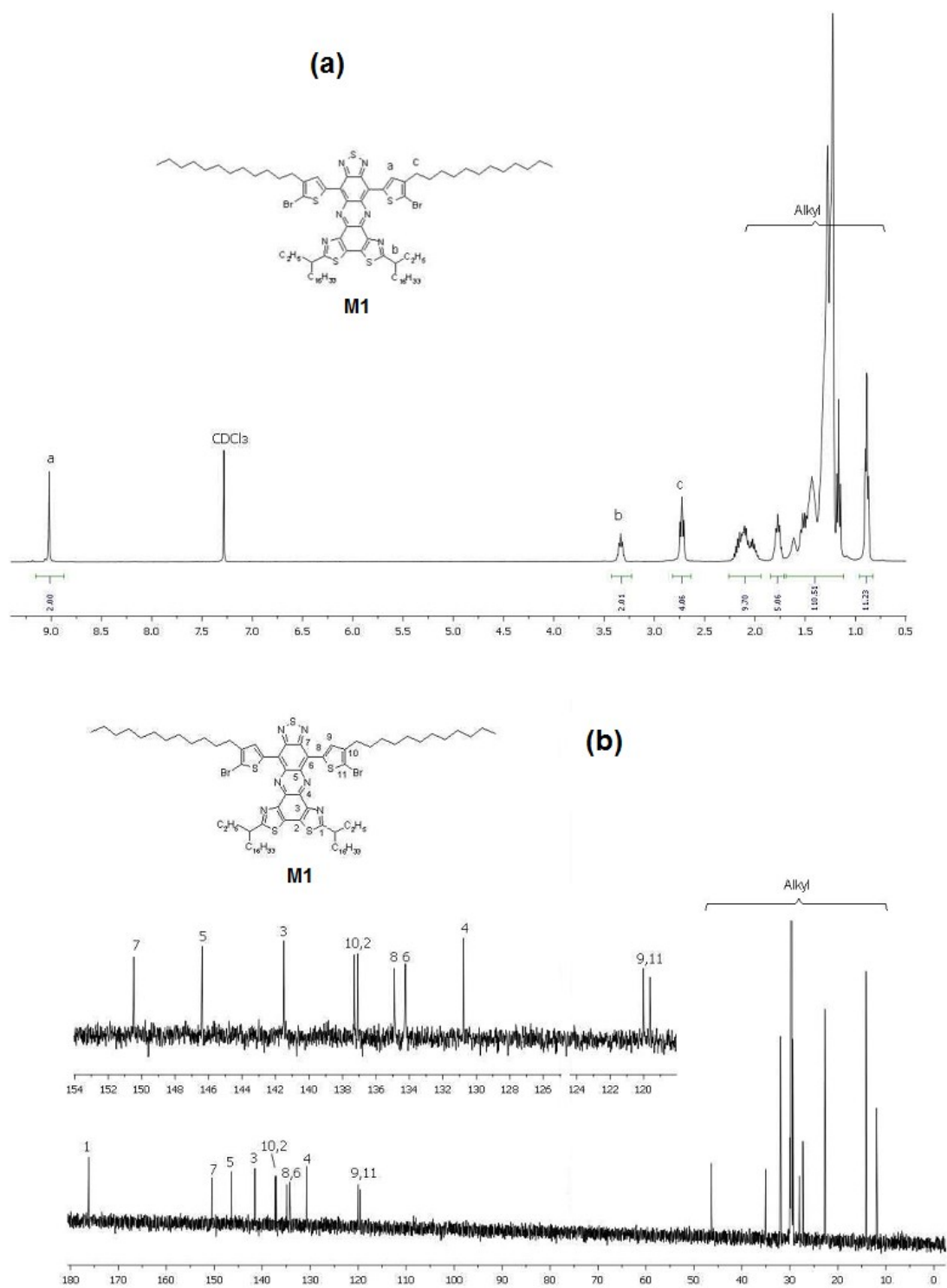


Figure S12 ^1H (a) and ^{13}C (b) NMR spectra for monomer **M1**

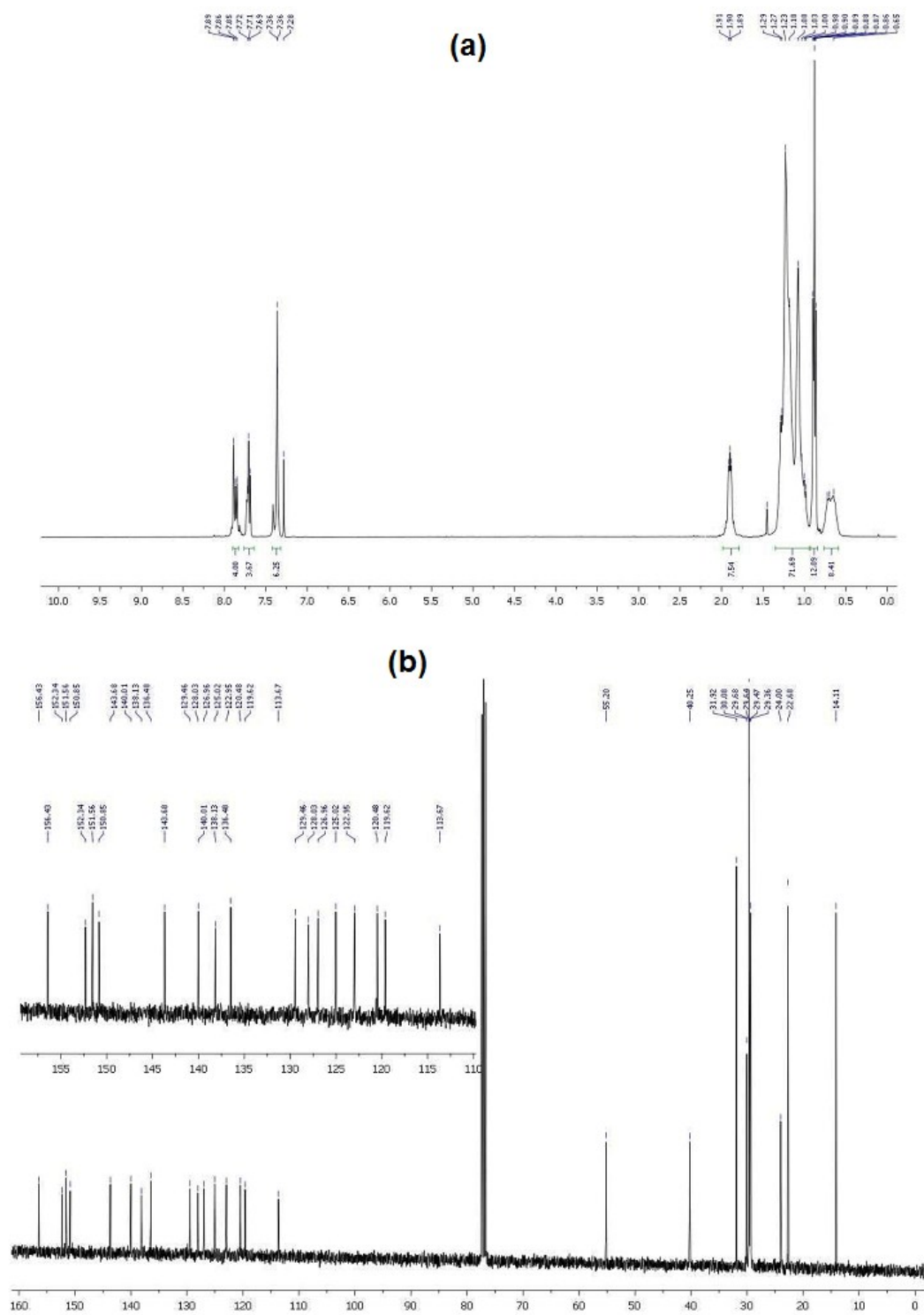


Figure S13 ^1H (a) and ^{13}C (b) NMR spectra for monomer **M2**

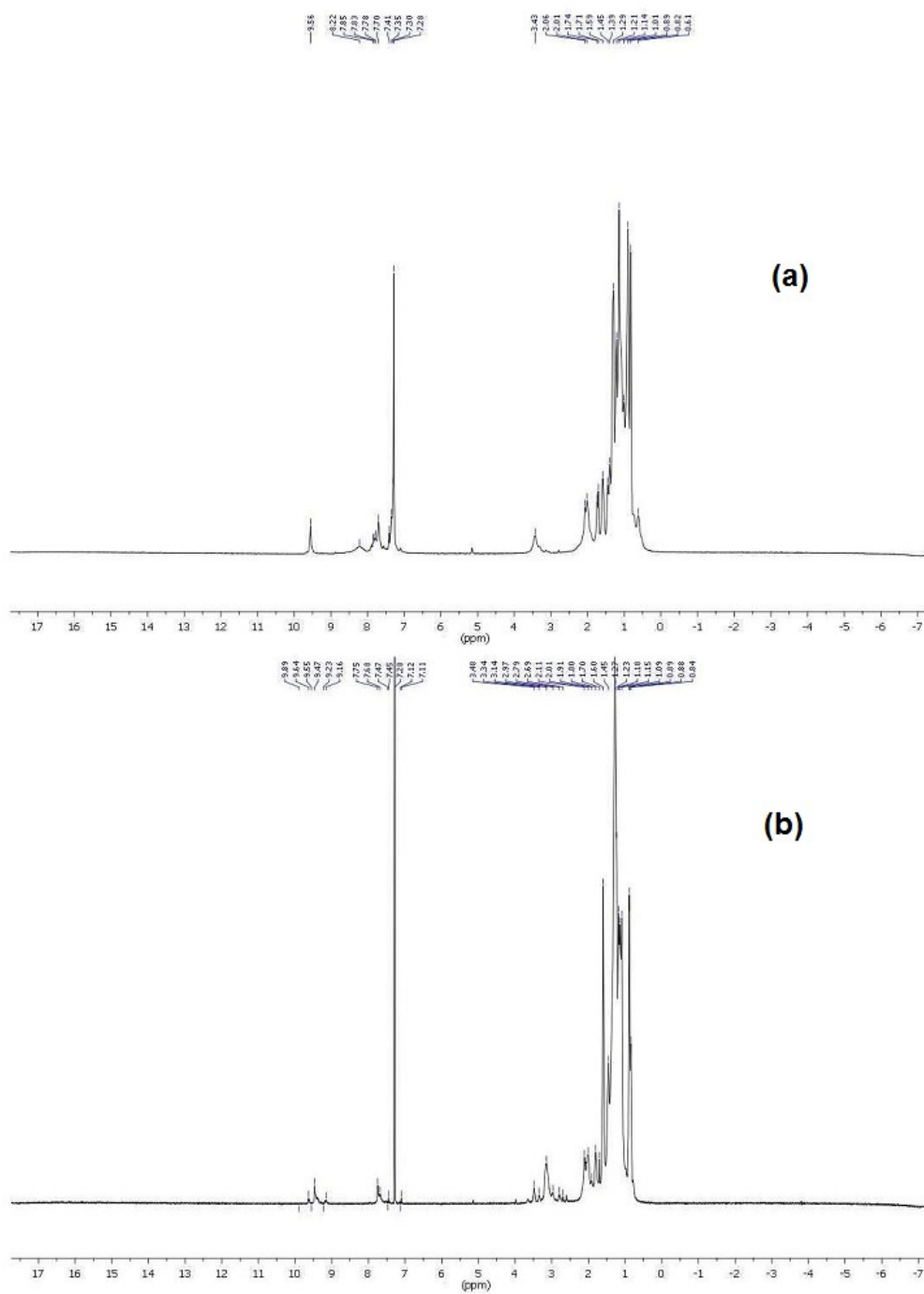


Figure S14 ^1H NMR spectra of (a) **F1** and (b) **F2** copolymers

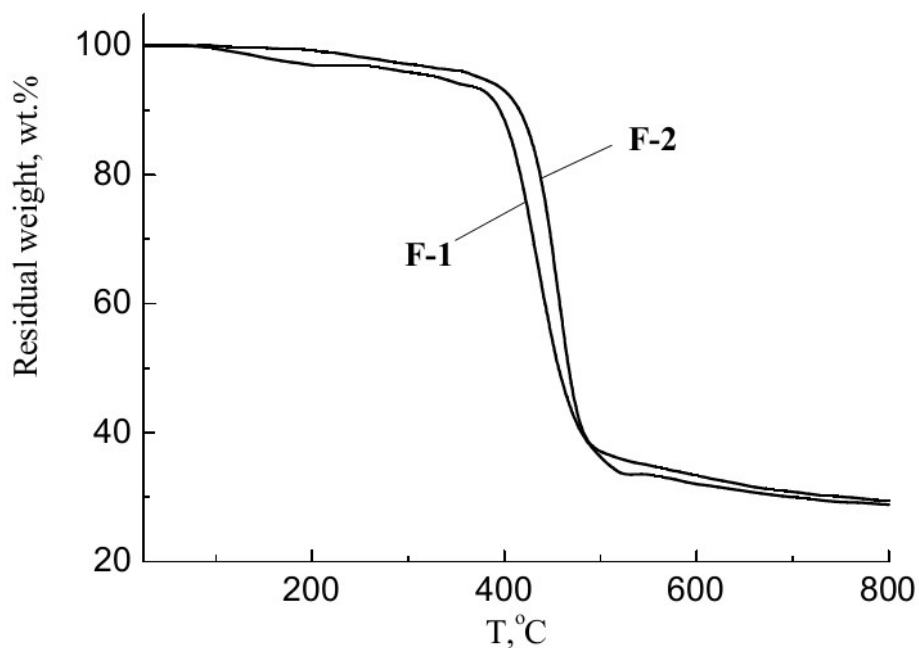


Figure S15 TGA curves polymers with a heating rate of $10^{\circ}\text{C min}^{-1}$ under an inert atmosphere

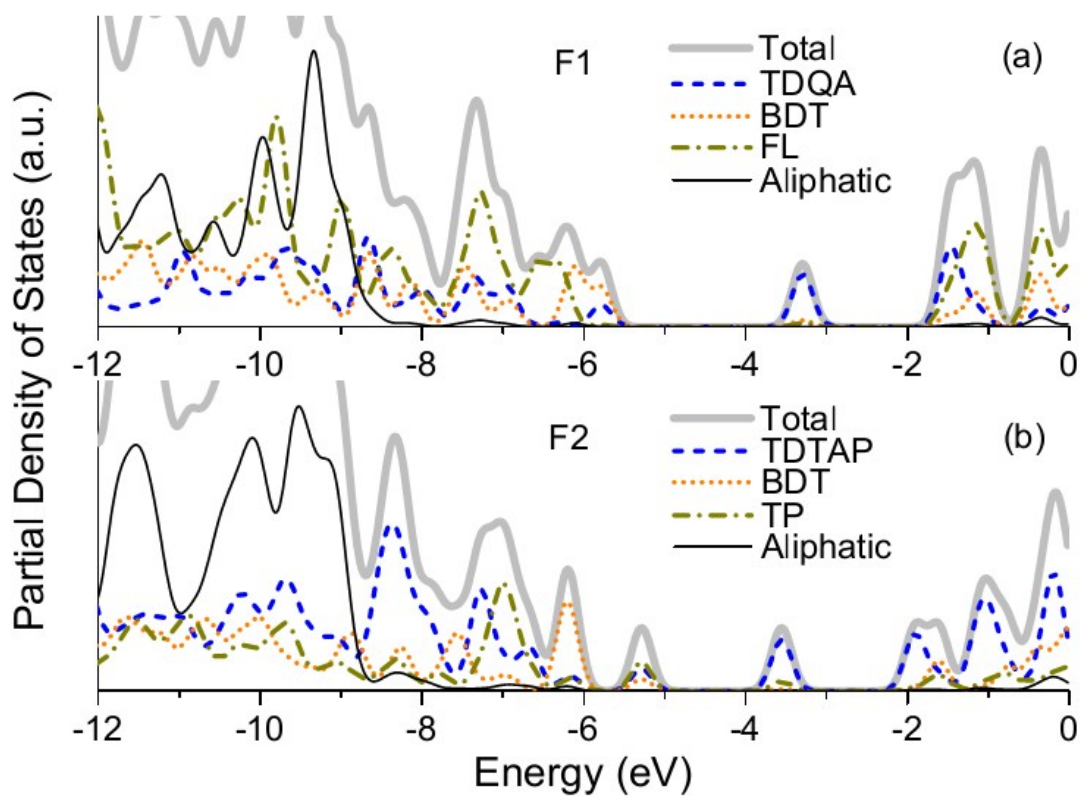


Figure S16 Total and partial density of states of (a) **F1**, and (b) **F2** (calculated using the M06 functional).

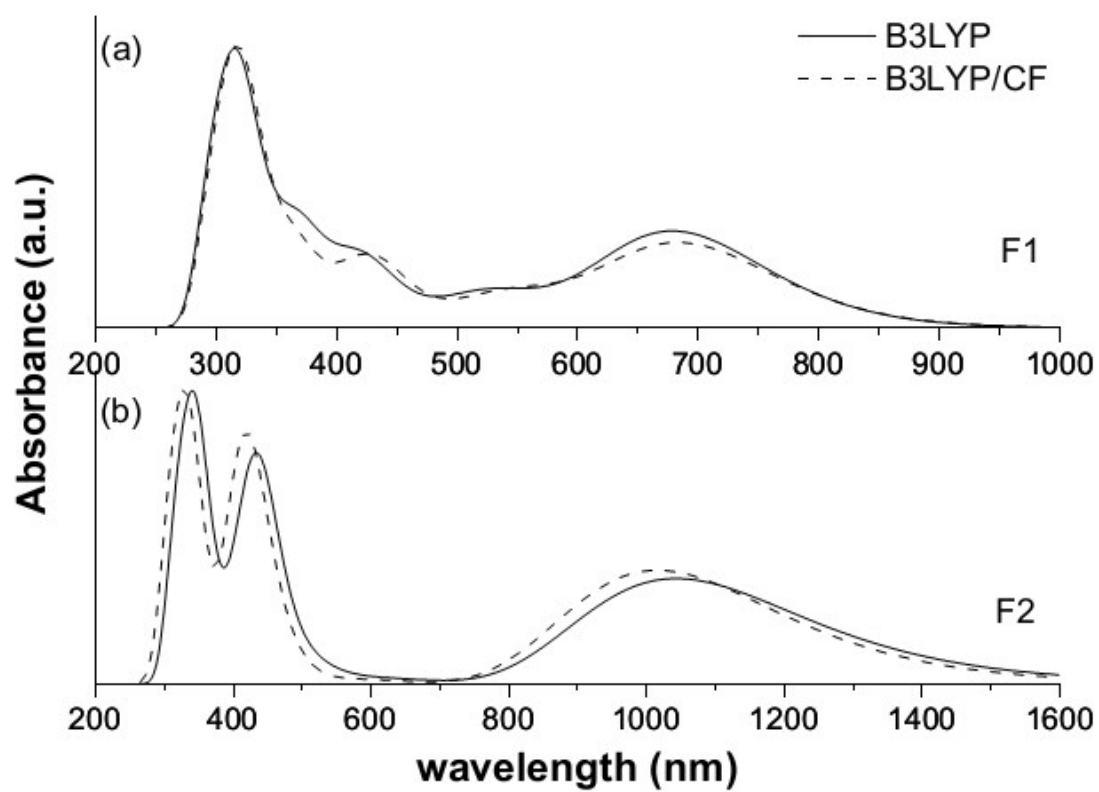


Figure S17 Theoretical UV/Vis absorption spectrum of (a) **F1**, and (b) **F2** (calculated using the B3LYP functional).