Supporting Information

Tuning Morphology and Photovoltaic Property of Diketopyrrolopyrrole-Based Small-Molecule Solar Cells by Taloring End-Capped Aromatic Groups

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Contents

1. Experimental section

1.1 Measurements and characterizations.

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AVANCE 400 MHz (or 400 MHz) spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III mass spectrometer. Elemental analysis was performed on a flash EA1112 analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 at a heating rate of 10 ℃/min under nitrogen flow. UV-vis absorption was recorded on a Hitachi U-3010 spectrometer. The electrochemical measurements were carried out in a deoxygenated solution of tetra-n-butylammonium hexafluorophosphate (0.1 M) in $CHCl_3$ with a computer-controlled Zennium electrochemical workstation. A glassy carbon electrode, a Pt wire, and an Ag/AgCl electrode were used as the working, counter, and reference electrodes, respectively. AFM images were obtained from the photovoltaic device samples using a Nanoscope V AFM (Digital Instruments) in tapping mode. TEM tests were performed on a JEM-2011F operated at 200 kV. The TEM specimens were prepared by transferring the spin-coated films to the 200 mesh copper grids. The XRD pattern was recorded by a Rigaku D/max–2500 diffractometer operated at 40 kV voltage and a 200 mA current with Cu Kα radiation.

1.2 Fabrications and characterizations of organic solar cells.

The organic solar cells (OSCs) devices were fabricated with the traditional configurations of ITO/PEDOT: PSS/Polymer/PCBM/Ca/Al. The indium tin oxide (ITO) glass was precleaned, respectively, with deionized water, acetone and isopropanol and treated in a Novascan PSD-ultraviolet-ozone chamber for 30 min. A thin layer (ca. 30 nm) of poly(3,4-ethylene-dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron P VP AI 4083, Germany) was spin-coated onto the ITO glass with spin-coating speed of 2000 rpm and baked at 150 ℃ for 10 min. A solution of compounds/$PC_{71}BM$ with ODCB, and ODCB-DIO as solvent, respectively, was subsequently spin-coated on the surface of the PEDOT: PSS layer to form a photosensitive layer. Then, the Ca/Al cathode was deposited on the photoactive layer by vacuum evaporation (ca. 20/80 nm). The effective area of one cell is 6 mm^2. The current-voltage (I-V) measurement of the devices was conducted on a computer-controlled Keithley 2400 Source Measure Unit. A xenon lamp with AM1.5 filter was used as the white light source, and the optical power at the sample was 100 mW/cm^2. EQE measurements were carried out on an oriel IQE 200 (Newport).

1.3 Tests of the hole mobilities.

The devices were fabricated with configuration of ITO/PEDOT: PSS/BDT-DPP: $PC_{71}BM$/Au. The active layers were spin-coated with ODCB and ODCB-DIO, respectively. The following equation was applied to estimate the hole mobilities:[1,2] $JL^3V^2)$ $=0.89(1/E_0)^{0.5}(V/L)^{0.5}+Ln(9\varepsilon\varepsilon_0\mu_0/ 8)$, where ε is the dielectric constant of the polymer, ε_0 the permittivity of the vacuum, μ_0 the zero-field mobility, E_0 the characteristic field, J the current density, L the thickness of the films, and $V = V_{\mathrm{appl}}-V_{\mathrm{bi}}$; V_{appl} is the applied potential, and V_{bi} the built-in potential which results from the difference in the work function of the anode and the cathode (in this device structure, $V_{\mathrm{bi}} = 0.2$ V). The hole mobility of the blending films were deduced from the intercept value $Ln(9\varepsilon\varepsilon_0\mu_0/ 8)$. Herein ε is 3, ε_0 is 8.85419×10^{-12} $CV^{-1}m^{-1}$.

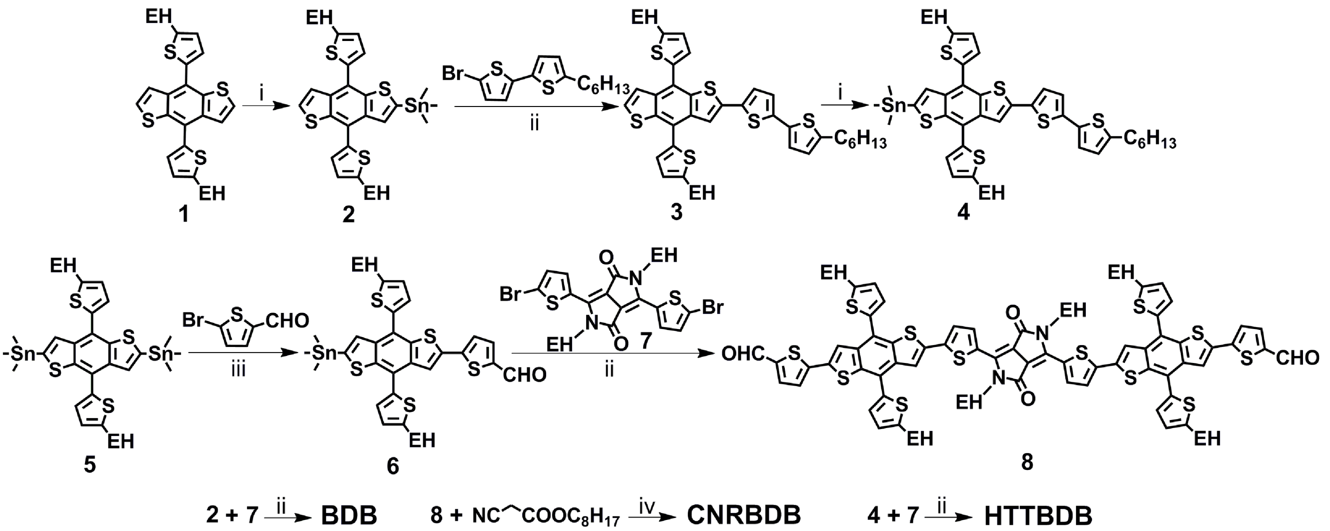
1.4. DFT calculations

Density functional theory (DFT) calculations were performed using the Gaussian 03 program[1] with the B3LYP exchange-correlation functional.[3-5] All-electron triple-ξ valence basis sets with polarization functions (6-311G**) are used for all atoms. Geometry optimizations were performed with full relaxation of all atoms. For each molecule, various conformations with different dihedral angles were optimized, and the data for the one with the lowest energy are reported.

2. Synthesis

2.1. Materials.

All of the starting materials and solvents were purchased from Sigma Aldrich or Alfa Aesar and were used without further purification, unless stated otherwise. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl under nitrogen before use. The starting material of 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (**1**) and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**5**) was purchased from Solarmer and 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**7**) was purchased from Suna Tech Inc.



Reaction conditions: (i) *n*–BuLi, –78 °C, 1 hrs; then $(CH)_3SnCl$, rt, 2 hrs. (ii) $Pd(PPh_3)_4$, toluene, 110°C, 24 hrs. (iii) $Pd(PPh_3)_4$, toluene, 110°C, 5 hrs. (iv) $CHCl_3$, piperidine, RT, 36 hrs. EH = 2-ethylhexyl.

Scheme S1 Synthetic routes of **BDB**, **CNRBDB** and **HTTBDB**.

2.2. Materials Synthesis and Characterizations.

The synthesis routes to **BDB**, **CNRDBD** and **HTTBDT** are shown in Scheme S1. The detailed synthetic processes are as follows.

2-(5'-hexyl-[2,2'-bithiophen]-5-yl)-4,8-bis(5-octylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (3). Under protection of argon at –70 °C, 1.6 M n-butyllithium solution in hexanes (0.6 mL, 1 mmol) was added dropwise to 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (**1**) (578 mg, 1 mmol) dissolved in 25 mL of THF. The solution was warmed to room temperature for 1 h, and then 1.0 M trimethyltin chloride solution in THF (1.3 mL, 1.3 mmol) was added. The reaction mixture was poured into water (50 mL) and extracted with EtOAc (50 mL). The organic phase was evaporated to afford a yellow oil (**2**) (*ca*. 700 mg) which was used for the next step without further purification. Following the representative general procedure for stilling coupling reaction, 205 mg of 5-bromo-5'-hexyl-2,2'-bithiophene (0.62 mmol) was reacted with the yellow oil (700 mg) in the presence of $Pd(PPh_3)_4$ (25 mg) and toluene (20 mL). After refluxing the mixture for 12 h, the mixture was poured in water (50 mL) and extracted with CH_2Cl_2 (50 mL). The organic layer was dried over anhydrous sodium sulfate and removed under reduced pressure. The crude product is purified by column chromatography on a silica gel with chloroform/hexane, giving 330 mg of yellow oil (**3**) (65%). ^{1}H NMR (400 MHz, CD_2Cl_2 , δ): 7.68 (1H, s), 7.62 (1H, d, *J* = 8.0 Hz), 7.50 (1H, d, *J* = 8.0 Hz), 7.33 (3H, t, *J* = 4.0 Hz), 7.20 (1H, d, *J* = 4.0 Hz), 7.06 (1H, d, *J* = 4.0 Hz), 7.03 (1H, d, *J* = 4.0 Hz), 6.96 (2H, t, *J* = 4.0 Hz), 6.72 (1H, d, *J* = 4.0 Hz), 2.89–2.92 (4H, d, *J* = 4.0 Hz), 2.80–2.83 (2H, t, *J* = 8.0 Hz), 1.63–1.73 (4H, m), 1.27–1.48 (22H, m), 0.89–1.00 (15H, m).

(6-(5'-hexyl-[2,2'-bithiophen]-5-yl)-4,8-bis(5-octylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl) trimethylstannane (4). Under protection of argon at –70 °C, 1.6 M n-butyllithium solution in hexanes (0.3 mL, 0.48 mmol) was added dropwise to **3** (330 mg, 0.4 mmol) dissolved in 25 mL of THF. The solution was warmed to room temperature for 1 h, and then 1.0 M trimethyltin chloride solution in THF (1.3 mL, 1.3 mmol) was added. The reaction mixture was poured into water (50 mL) and extracted with EtOAc (50 mL). The organic phase was evaporated to afford a yellow oil (**4**) (*ca*. 390 mg) which was used for the next step without further purification.

5-(4,8-bis(5-octylthiophen-2-yl)-6-(trimethylstannyl)benzo[1,2-b:4,5-b']dithiophen-2-yl)thiophene-2-carbaldehyde (6). Following the representative general procedure for stilling coupling reaction, 904 mg of **5** (1.0 mmol) is reacted with 5-bromothiophene-2-carbaldehyde (95 mg, 0.5 mmol) in the presence of $Pd(PPh_3)_4$ (25 mg) and toluene (15 mL). After refluxing the mixture for 5 h, the mixture was poured into water (50 mL) and extracted with CH_2Cl_2 (50 mL). The organic layer was dried over anhydrous sodium sulfate and removed under reduced pressure. The crude product was purified by column chromatography on a silica gel with dichloromethane/hexane, giving 277 mg of a yellow oil (**6**) (65%). ^{1}H NMR (400 MHz, CD_2Cl_2 , δ): 9.88 (1H, s), 7.53 (1H, s), 7.72 (1H, d, J = 4.0 Hz), 7.70 (1H, s), 7.39 (1H, d, J = 4.0 Hz), 7.34 (2H, d, J = 4.0 Hz), 6.97 (2H, d, J = 4.0 Hz), 2.90 (4H, d, J = 8.0 Hz), 1.68–1.77 (2H, m), 0.35–0.49 (9H, s).

5,5'-(6,6'-(5,5'-(2,5-dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis(thiophene-5,2-diyl))bis(4,8-bis(5-octylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-6,2-diyl))bis(thiophene-2-carbaldehyde) (**8**). Following the representative general procedure for stilling coupling reaction, 277 mg of **6** (0.33 mmol) was reacted with **7** (88 mg, 0.13 mmol) in the presence of $Pd(PPh_3)_4$ (25 mg) and toluene (20 mL). After refluxing the mixture for 12 h, the mixture was poured in water (50 mL) and extracted with CH_2Cl_2 (50 mL). The organic layer was dried over anhydrous sodium sulfate and removed under reduced pressure. The crude product is simply purified by column chromatography on a silica gel with chloroform/methanol, giving 180 mg of a black solid (**8**) (78%).

3,6-bis(5-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (BDB). Following the representative general procedure for stilling coupling reaction, **6** (325 mg, 0.44 mmol) was reacted with **7** (100 mg, 0.13 mmol) in the presence of $Pd(PPh_3)_4$ (25 mg) and toluene (20 mL). After refluxing the mixture for 12 h, the mixture was poured in water (50 mL) and extracted with CH_2Cl_2 (50 mL). The organic layer was dried over anhydrous sodium sulfate and removed under reduced pressure. The crude product is purified by column chromatography on a silica gel with chloroform/methanol, giving 170 mg of a black solid (**BDB**) (70%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.94 (2H, d, J = 4.0 Hz), 7.83 (2H, s), 7.61 (2H, d, J = 8.0 Hz), 7.46 (2H, d, J = 8.0 Hz), 7.40 (2H, d, J = 4.0 Hz), 7.32 (2H, d, J = 4.0 Hz), 7.30 (2H, d, J = 4.0 Hz), 6.92 (2H, d, J = 4.0 Hz), 6.92 (4H, t, J = 4.0 Hz), 4.05 (4H, m), 2.88 (8H, m), 1.92 (2H, m),1.72 (2H, m), 1.27–1.49 (48H, m), 0.83–0.98 (36H, m). ^{13}C NMR (500

MHz, $CDCl_3$): δ 161.58, 146.11, 146.06, 142.67, 139.59, 139.35, 138.63, 137.23, 136.75, 136.37, 129.25, 128.00, 127.81, 126.15, 125.53, 125.48, 124.36, 123.75, 123.52, 120.83, 108.69, 77.27, 77.02, 76.76, 45.98, 41.48, 39.32, 34.33, 32.57, 32.53, 31.45, 30.40, 29.71, 28.95, 28.56, 25.76, 23.75, 23.10, 23.05, 14.18, 14.08, 10.93, 10.64. MALDI-TOF MS: calcd for $C_{98}H_{120}N_2O_2S_{10}$ 1676.6; found 1677.0. Anal. calcd for $C_{98}H_{120}N_2O_2S_{10}$: C, 70.12%, H, 7.21%, N, 1.67%. Found: C, 70.08%, H, 7.24%, N, 1.66%.

(2E,2'E)-dioctyl3,3'-(5,5'-(6,6'-(5,5'-(2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis(thiophene-5,2-diyl))bis(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-6,2-diyl))bis(thiophene-5,2-diyl))bis(2-cyanoacrylate) (CNRBDB). Octyl cyanoacetate (0.90 mL, 1.00 mmol) was added to a solution of **8** (180 mg, 0.10 mmol) and triethylamine (3 drops) in dry $CHCl_3$ (50 mL) and then the solution was stirred for 36 h under N_2 at room temperature. Water was added and the reaction mixture was extracted with CH_2Cl_2 , the combined extracts were washed three times with water and then dried ($MgSO_4$). The solvent was evaporated under reduced pressure and the crude product further purified through column chromatography (hexane/CH_2Cl_2) and subsequently washed with hexane and acetone to afford a dark powder (207 mg, 92%). ^{1}H NMR (400 MHz, CD_2Cl_2 , δ): 9.08 (2H, d, *J* = 4.0 Hz), 8.00 (2H, s), 7.57 (4H, s), 7.52 (2H, s), 7.37 (2H, d, *J* = 4.0 Hz), 7.32 (2H, d, *J* = 4.0 Hz), 7.16–7.20 (4H, m), 6.98–7.03 (4H, m), 4.20 (4H, t, *J* = 4.0 Hz), 3.81–4.00 (4H, m), 3.00 (8H, d, *J* = 8.0 Hz), 1.72–1.91 (10H, m), 1.24–1.44 (68H, m), 0.80–1.07 (42H, m). ^{13}C NMR (500 MHz, $CDCl_3$): δ 162.63, 160.95, 146.36, 146.26, 145.15, 139.09, 139.06, 138.92, 138.86, 138.45, 137.37, 137.20, 137.00, 136.86, 136.33, 136.02, 135.72, 131.57, 128.19, 125.79, 125.58, 123.88, 123.34, 123.20, 121.73, 120.01, 119.92, 115.74, 108.35, 108.28, 93.20, 77.27, 77.02, 76.77, 66.60, 41.34, 39.39, 34.53, 32.70, 31.80, 30.34, 29.23, 29.19, 29.01, 28.56, 25.80, 23.16, 22.67, 14.27, 14.18, 14.11, 10.93, 10.62. MALDI-TOF MS: calcd for $C_{130}H_{158}N_4O_6S_{12}$ 2254.9; found 2256.0. Anal. calcd for $C_{130}H_{158}N_4O_6S_{12}$: C, 69.17%, H, 7.05%, N, 2.48%. Found: C, 69.15%, H, 7.06%, N, 2.47%.

3,6-bis(5-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-6-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (HTTBDB). Following the representative general procedure for stilling coupling reaction, **4** (300 mg, 0.30 mmol) was reacted with **7** (68 mg, 0.10 mmol) in the presence of $Pd(PPh_3)_4$ (25 mg) and toluene (20 mL). After refluxing the mixture for 12 h, the mixture was poured in water (50 mL) and extracted with CH_2Cl_2 (50 mL). The organic layer was dried over anhydrous sodium sulfate and removed under reduced pressure. The crude product is purified by column chromatography on a silica gel with chloroform/methanol, giving 130 mg of a black solid (**HTTBDB**) (60%).^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.07 (2H, d, *J* = 4.0 Hz), 7.58 (2H, s), 7.35 (4H, d, *J* = 4.0 Hz), 7.31 (2H, d, *J* = 4.0 Hz), 7.21 (2H, d, *J* = 4.0 Hz), 6.95 (4H, d, *J* = 4.0 Hz), 6.89 (2H, s), 6.86 (2H, d, *J* = 4.0 Hz), 6.80 (2H, s), 6.60 (2H, d, *J* = 4.0 Hz), 3.90–4.05 (4H, m), 2.95 (8H, d, *J* = 4.0 Hz), 2.70 (4H, t, *J* = 8.0 Hz), 1.75–1.87 (10H, m), 1.25–1.48 (60H, m), 0.83–1.10 (42H, m). ^{13}C NMR (600 MHz, $CDCl_3$): δ 161.16, 145.84, 145.74, 142.23, 138.71, 138.41, 137.93, 137.79, 137.12, 136.93, 136.84, 136.52, 135.85, 134.93, 134.41, 128.56, 127.99, 127.88, 125.56, 125.40, 124.62, 123.31, 123.11, 122.82, 120.28, 118.40, 108.27, 77.27, 77.02, 76.77, 45.87, 41.46, 39.44, 34.48, 32.66, 31.58, 31.40, 30.41, 30.15, 29.71, 29.03, 28.88, 28.54, 25.83, 25.79, 23.74, 23.16, 22.61, 14.27, 14.16, 14.09, 11.00, 10.95, 10.67. MALDI-TOF MS: calcd for $C_{126}H_{152}N_2O_2S_{14}$ 2172.8; found 2173.0. Anal. calcd for $C_{126}H_{152}N_2O_2S_{14}$: C, 69.56%, H, 7.04%, N, 1.29%. Found: C, 69.55%, H, 7.05%, N, 1.27%.

3. Supporting figures

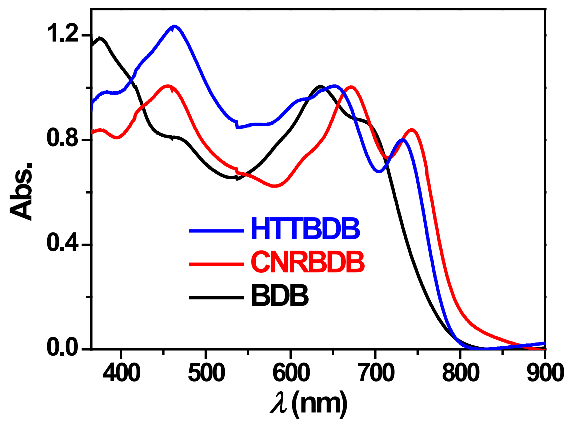


Fig. S1 Absorption spectrum of the three molecules blended films.

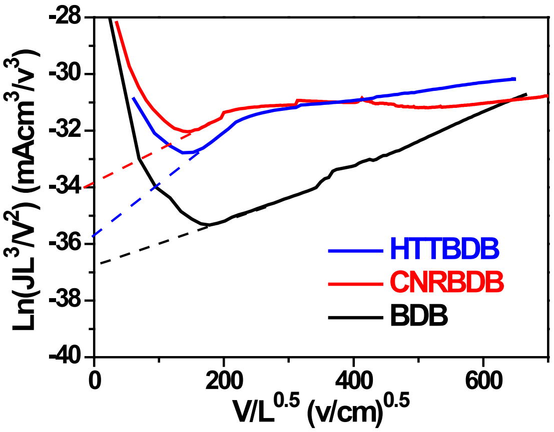


Fig. S2 Plots of Ln(JL^3/V^2) vs. $(V/L)^{0.5}$ of compounds/PC$_{71}$BM. The device structures are ITO/PEDOT: PSS/Donors: PC$_{71}$BM/Ca/Al.

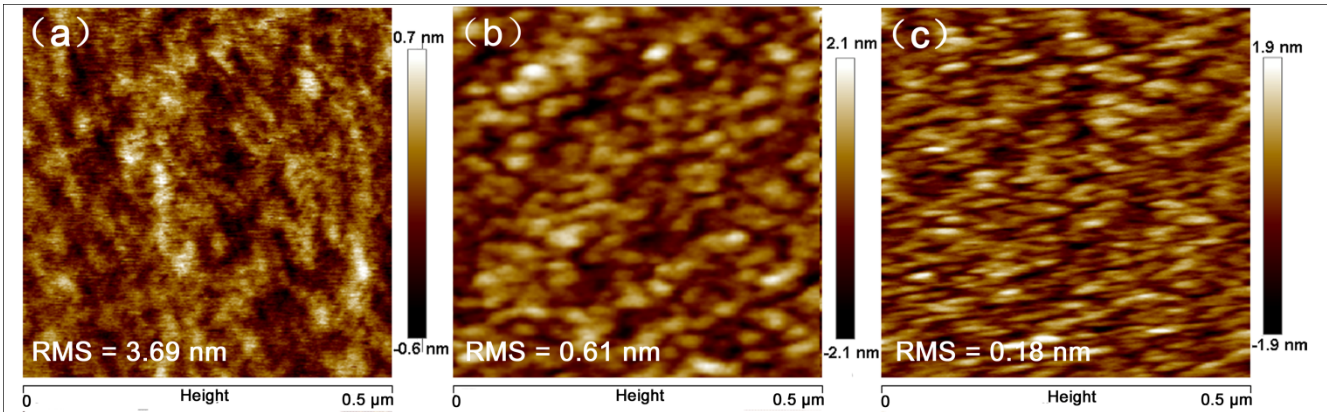


Fig. S3 AFM height images of the **BDB**/PC$_{71}$BM (a), **CNRBDB**/PC$_{71}$BM (b) and **HTTBDB**/PC$_{71}$BM (c), respectively.

Table S1. The experimental and calculated HOMO/LUMO energy levels and band gaps using the DFT calculations.

	HOMO		LUMO		E_g^{cv} (eV)	E_g^{DFT} (eV)
	CV (eV)	DFT (eV)	CV (eV)	DFT (eV)		
BDB	-5.16	-4.74	-3.60	-2.73	1.56	2.01
CNRBDB	-5.17	-4.90	-3.67	-3.04	1.50	1.86
HTTBDB	-5.13	-4.64	-3.58	-2.73	1.55	1.91

Table S2. Photovoltaic performances base on the **BDB**/$PC_{71}BM$ blend.

D/A ratio	DIO (v/v)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (avg %)
2:1	0	1.31	0.89	0.24	0.26 (0.21)
1:1	0	4.22	0.78	0.27	0.91 (0.86)
1:1	0.1%	3.20	0.83	0.27	0.73(0.70)
1:1	0.2%	2.61	0.85	0.25	0.56(0.49)
1:1	0.3%	2.39	0.85	0.25	0.51(0.48)
1:2	0	2.63	0.82	0.26	0.52 (0.48)

Table S3. Photovoltaic performances base on the **CNRBDB**/$PC_{71}BM$ blend.

D/A ratio	DIO (v/v)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (avg %)
2:1	0	1.37	0.76	0.43	0.45 (0.40)
1:1	0%	1.64	0.75	0.52	0.64 (0.61)
1:1	0.1%	3.22	0.77	0.55	1.36 (1.29)
1:1	0.2%	3.44	0.78	0.57	1.52 (1.50)
1:1	0.3%	3.56	0.75	0.51	1.36 (1.26)
1:2	0	1.20	0.75	0.56	0.51 (0.47)

Table S4. Photovoltaic performances base on the **HTTBDB**/$PC_{71}BM$ blend.

D/A ratio	DIO (v/v)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (avg %)
2:1	0	2.92	0.68	0.30	0.37 (0.32)
1:1	0	6.22	0.70	0.38	1.65 (1.59)
1:1	0.1%	8.06	0.63	0.40	2.03 (2.00)
1:1	0.2%	9.66	0.64	0.46	2.85 (2.81)
1:1	0.3%	6.06	0.60	0.42	1.52 (1.46)
2:1	0	2.92	0.68	0.30	0.60 (0.53)

NMR data

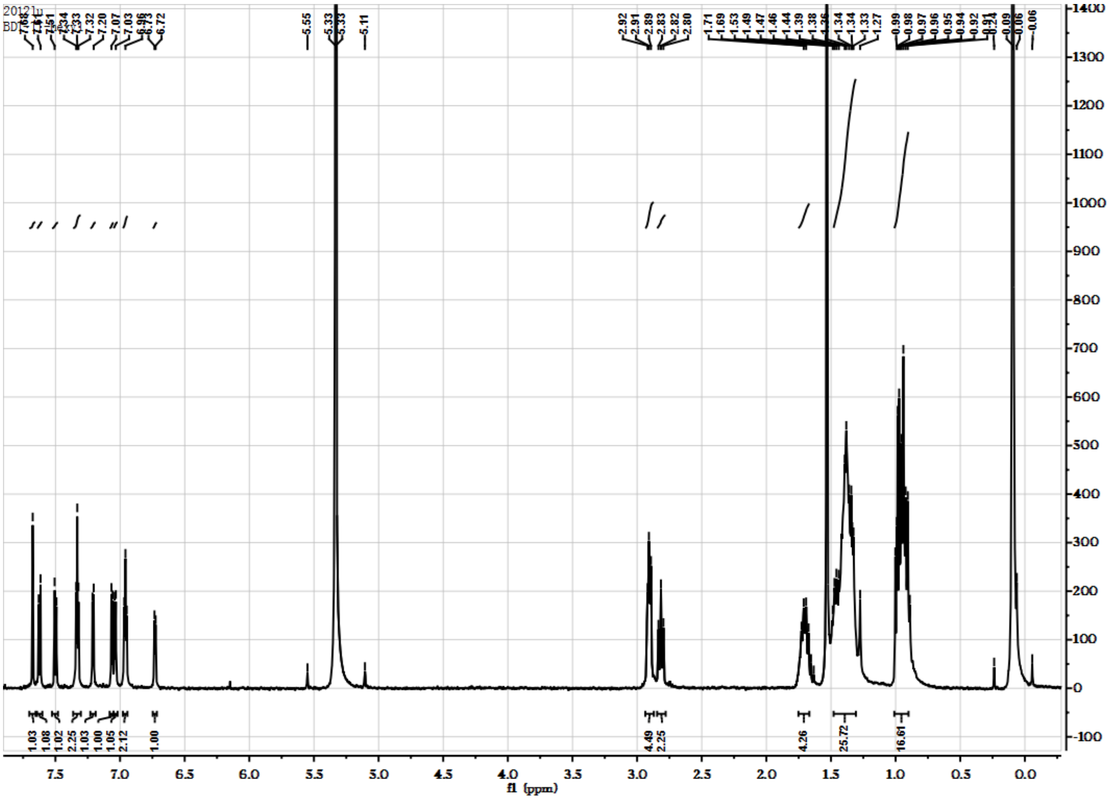


Fig. S5 ^{1}H NMR spectra of **3**.

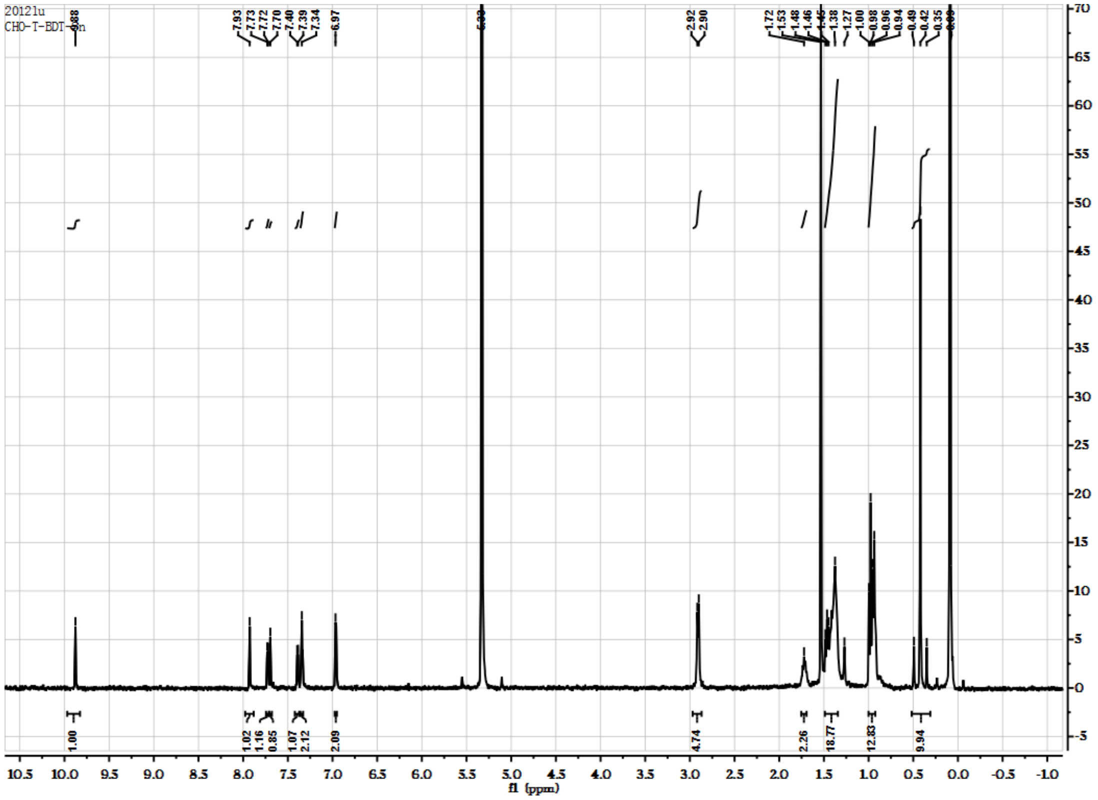


Fig. S6 ^{1}H NMR spectra of **6**.

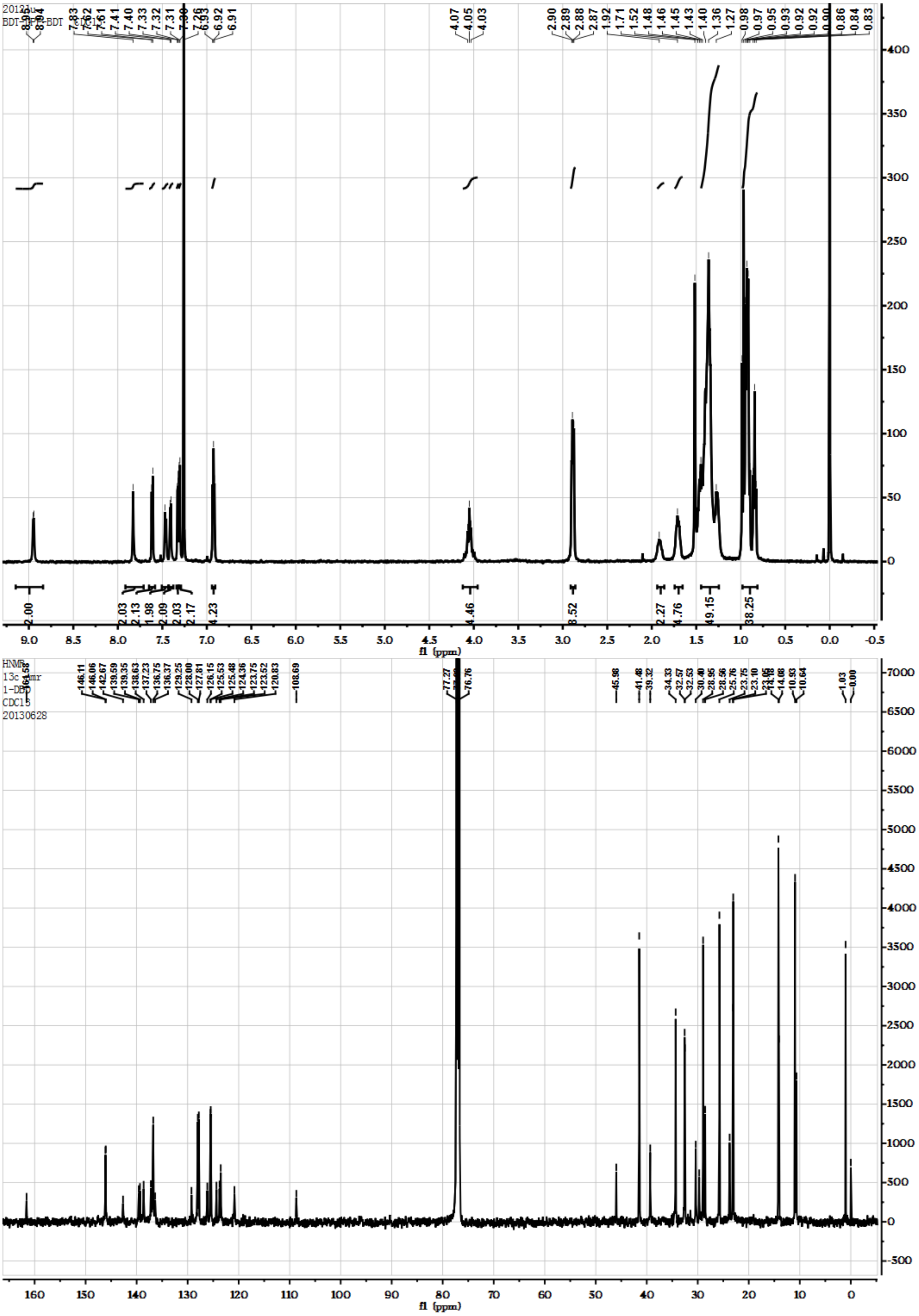
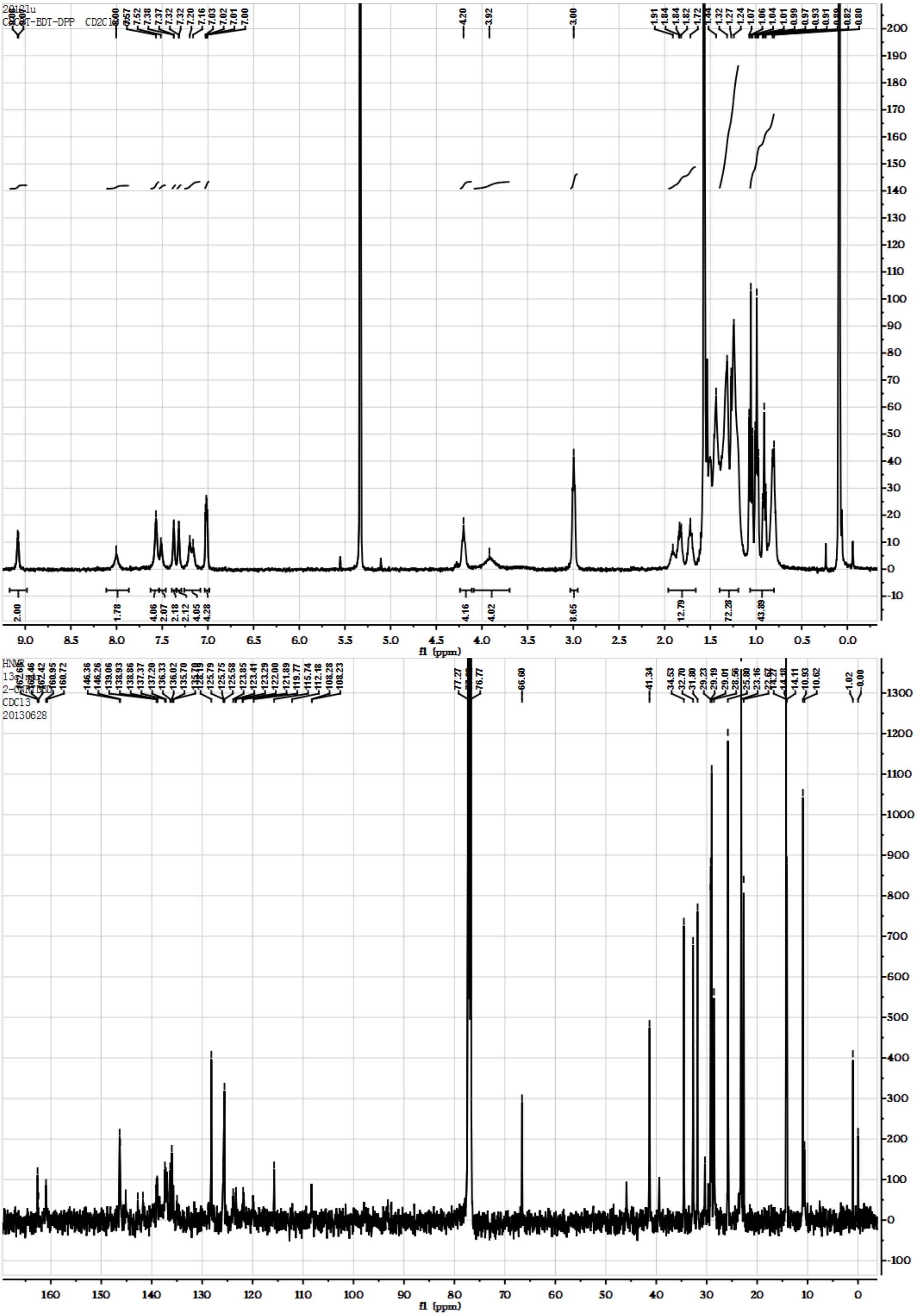


Fig. S7 ^{1}H NMR and ^{13}C NMR spectra of **BDB**.



5 **Fig. S8** ^{1}H NMR and ^{13}C NMR spectra of **CNRBDB**.

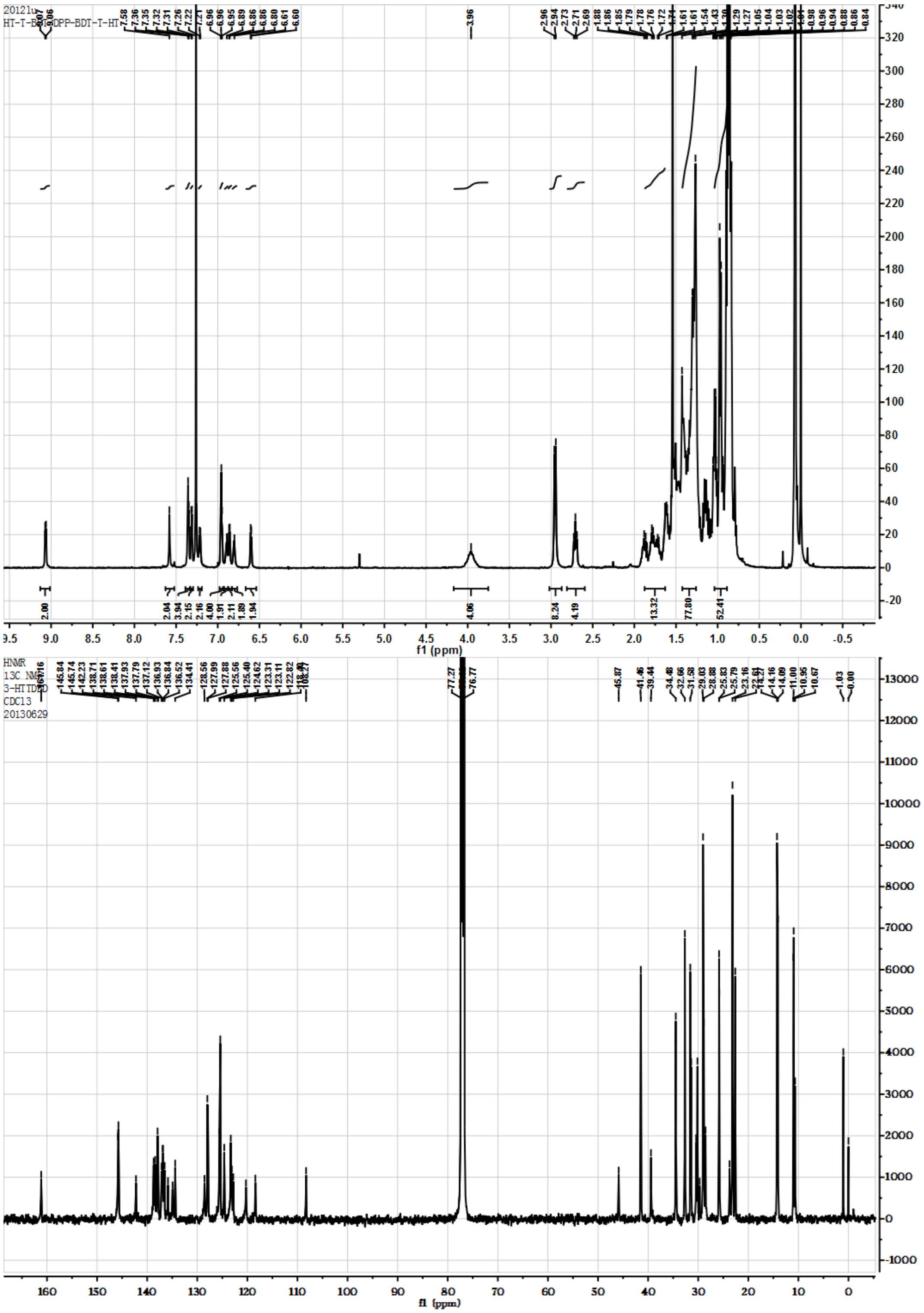


Fig. S9 ^{1}H NMR and ^{13}C NMR spectra of **HTTBDB**.

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