

Supporting Information

High-Performance n-Type Organic Thermoelectrics Enabled by Modulating the Cyano-Functionalized Polythiophene Backbones

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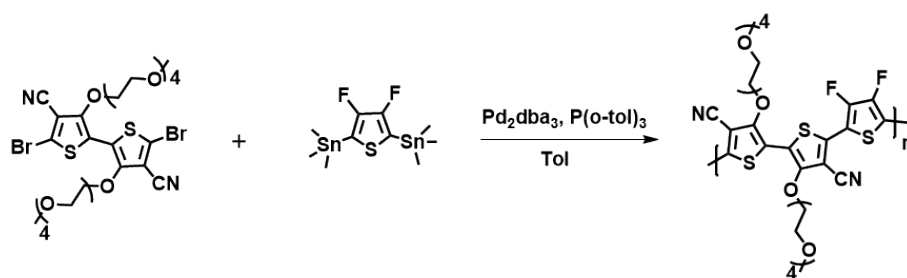
† J.W and S.M. contributed equally to this work.

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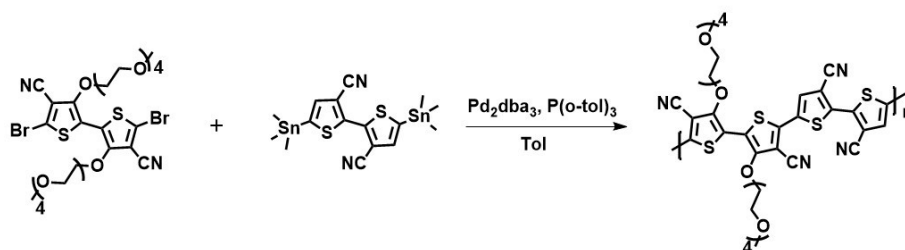
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1. Materials Synthesis

The reagents and chemicals were purchased from Admas-beta, and Bide pharmatch Ltd., etc, and the monomer 2FT-2Sn and CNT2-2Sn were synthesized according to the published protocols in literature^{1, 2}. The synthetic procedures for both polymers are shown as follow.



Synthesis of polymer CNg4T2-2FT. To a flame-dried glass tube was charged with monomer CNg4T2-2Br (50 mg, 0.0635 mmol), monomer 2FT-2Sn (28.3 mg, 0.0635 mmol), $\text{Pd}_2(\text{dba})_3$ (0.9 mg), and $\text{P}(o\text{-tolyl})_3$ (2.3 mg). The tube was then subjected to three pump/purge cycles with argon, followed by addition of 3 mL of anhydrous toluene. Next, the tube was sealed under an argon flow and heated to 120 °C and stirred at this temperature for 40 min. When the mixture was cooled to room temperature, the solution was dropped into 80 mL methanol under vigorous stirring. The generated precipitates were collected and subjected to Soxhlet extraction using methanol, acetone, hexane, dichloromethane, and chloroform as the solvents. The final chloroform fraction was concentrated and precipitated into methanol. The precipitates were collected and dried under a vacuum to afford the product polymer CNg4T2-2FT. Molecular weight: $M_n = 24.78$ kDa; $M_w = 47.83$ kDa; $D = 1.93$.



Synthesis of polymer CNg4T2-CNT2. To a flame-dried glass tube was charged with monomer CNg4T2-2Br (50 mg, 0.0635 mmol), monomer CNT2-2Sn (34.6 mg, 0.0635 mmol), Pd₂(dba)₃ (0.9 mg), and P(*o*-tolyl)₃ (2.3 mg). Then the tube was subjected to three pump/purge cycles with argon, followed by the addition of 3 mL of anhydrous toluene. Next, the tube was sealed under an argon flow and heated to 120 °C and stirred at this temperature for 60 min. The mixture was cooled to room temperature, and the solution was dropped into 80 mL methanol under vigorous stirring. The generated precipitates were collected and subjected to Soxhlet extraction using methanol, acetone, hexane, dichloromethane, and chloroform as the solvents. The final chloroform fraction was concentrated and precipitated into methanol. The precipitates were collected and dried under vacuum to afford the product polymer CNg4T2-CNT2. Molecular weight: $M_n = 11.87$ kDa; $M_w = 16.02$ kDa; $D = 1.35$.

2. Materials Characterization

¹H and ¹³C NMR spectra were recorded on Bruker Ascend-400 spectrometers. The chemical shifts (δ) were reported in ppm relative to the internal tetramethylsilane (TMS) standard. Polymer Laboratories GPC-PL220 high temperature GPC/SEC system at 120 °C (vs polystyrene standards) was used to determine the polymer molecular weights using 1,2,4-trichlorobenzene as the eluent. Thermogravimetric

analysis (TGA) and differential scanning calorimetry (DSC) were conducted on a Mettler, STARe TA Instrument and DSC Mettler STARe System at a heating ramp of 10 °C min⁻¹ under a N₂ flow rate of 90 mL min⁻¹. UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Cyclic voltammetry (CV) measurements of polymer films were carried out on a CHI660 potentiostat/galvanostat electrochemical workstation at a scan rate of 50 mV s⁻¹ with 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate in acetonitrile as the supporting electrolyte, a platinum disk as working electrode, a platinum wire as the counter electrode, and the Ag/Ag⁺ as a reference electrode, and the ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as the reference for all measurements. Atomic force microscopy (AFM) was performed using a Dimension Icon Scanning Probe Microscope (Asylum Research, MFP-3D-Stand Alone) in tapping mode. Two-dimensional grazing incidence wide angle X-ray scattering (2D-GIWAXS) measurements were performed at the Beamline PLS-II 9A SAXS of Pohang Accelerator Laboratory, Republic of Korea.

3. Device Fabrication and Characterization

Electrical conductivity measurement. First, acetone and isopropyl alcohol were successively used for ultrasonic cleaning to clean the borosilicate glass sheet. It is then treated with UV-ozone. 30 nm Au electrodes were then thermally evaporated on top with a channel length of 100 μm and a channel width of 2 mm. Then AuNP was thermally evaporated on the whole glass sheet as a catalyst. In a nitrogen glove box, the materials were spin-coated from their chloroform solution (5 mg mL⁻¹) at a spin coating

rate of 1500 rpm for 60 s and annealed at 190°C for 10 minutes. Then *N*-DMBI solution with distinct concentration (0.5–5 mg mL⁻¹) was spin-coated at 1500 rpm for 60 s, followed by thermal annealing at 120 °C for 10 s to complete the doping reaction. The prepared devices were tested in the glove box using a probe stand connected to the Keithley 4200 SCS. Electrical conductivity performance was calculated using Ohm's law from linear *I-V* characteristics measured. All reported electrical conductivity values were the average of five different measurements.

Thermoelectric performance characterization. The sequentially doped polymer films were prepared using the same conditions for electrical conductivity measurement. For example, 30 nm Au electrodes were thermally evaporated on cleaned borosilicate glass substrates with a channel length of 1 mm, a channel width of 20 mm, and an electrode width of 500 μm. Using a pair of Peltier devices (separation distance: 1 mm), a pair of thermocouples monitor the temperature difference (ΔT) generated between electrodes. During the measurement process, ΔT was systematically varied in the range of 0 ~ 2.8 K (step:0.7 K). The Keithley 4200-SCS system was utilized to record the thermal voltage response curve, and the Seebeck coefficient was extracted by linear fitting the thermal voltage with ΔT data. All reported Seebeck coefficients are average values of three different measurements.

4. Supplementary Table

Table S1. 2D GIWAXS packing parameters of polymer films.

Polymer	Crystallographic parameters		As-cast	Annealed	Doped
CNg4T2-2FT	q_{xy} profile (010)	$q_{xy, (010)} (\text{\AA}^{-1})$	1.76E+00	1.77E+00	1.77E+00
		$d_{xy, (010)} (\text{\AA})$	3.57E+00	3.55E+00	3.55E+00
		FWHM (\AA^{-1})	8.86E-02	7.86E-02	7.78E-02
		$CCL_{xy, (010)} (\text{\AA})$	6.38E+01	7.19E+01	7.27E+01
	q_z profile (100)	$q_{z, (100)} (\text{\AA})$	2.96E-01	2.94E-01	2.82E-01
		$d_{z, (100)} (\text{\AA})$	2.12E+01	2.14E+01	2.22E+01
		FWHM (\AA^{-1})	3.67E-02	3.54E-02	2.80E-02
		$CCL_{z, (100)} (\text{\AA})$	1.54E+02	1.60E+02	2.02E+02
CNg4T2-CNT2	q_{xy} profile (010)	$q_{xy, (010)} (\text{\AA}^{-1})$	1.71E+00	1.71E+00	1.72E+00
		$d_{xy, (010)} (\text{\AA})$	3.67E+00	3.67E+00	3.65E+00
		FWHM (\AA^{-1})	1.80E-01	1.30E-01	1.16E-01
		$CCL_{xy, (010)} (\text{\AA})$	3.14E+01	4.34E+01	4.87E+01
	q_z profile (100)	$q_{z, (100)} (\text{\AA})$	3.54E-01	3.49E-01	3.26E-01
		$d_{z, (100)} (\text{\AA})$	1.78E+01	1.80E+01	1.93E+01
		FWHM (\AA^{-1})	6.06E-02	4.39E-02	3.90E-02
		$CCL_{z, (100)} (\text{\AA})$	9.33E+01	1.29E+02	1.45E+02

5. Supplementary Figures Materials

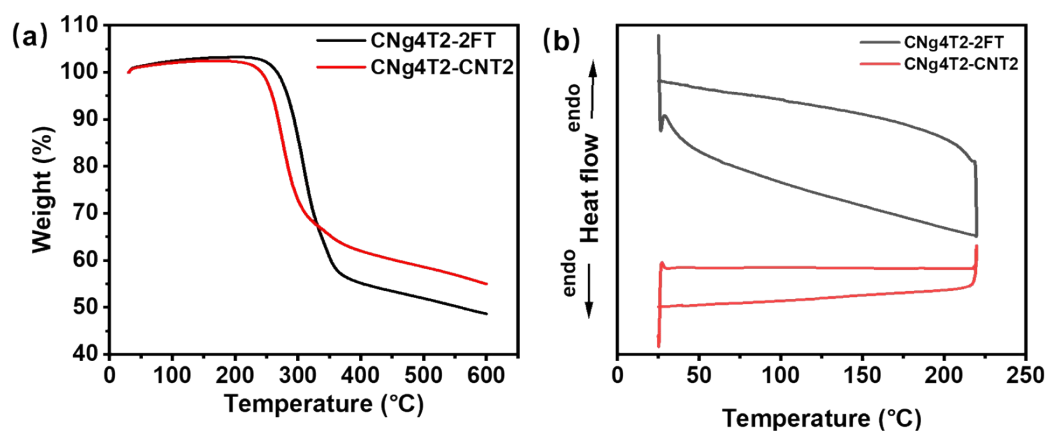


Figure S1. (a) Thermogravimetric (TGA) and (b) differential scanning calorimetry (DSC) curves of the polymers.

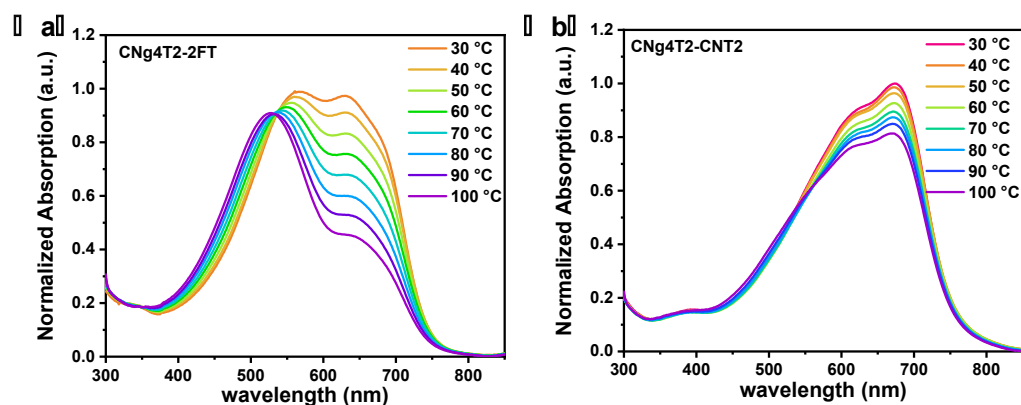


Figure S2. Temperature-dependent absorption spectra of (a) CNg4T2-2FT and (b) CNg4T2-CNT2 in diluted chlorobenzene solutions.

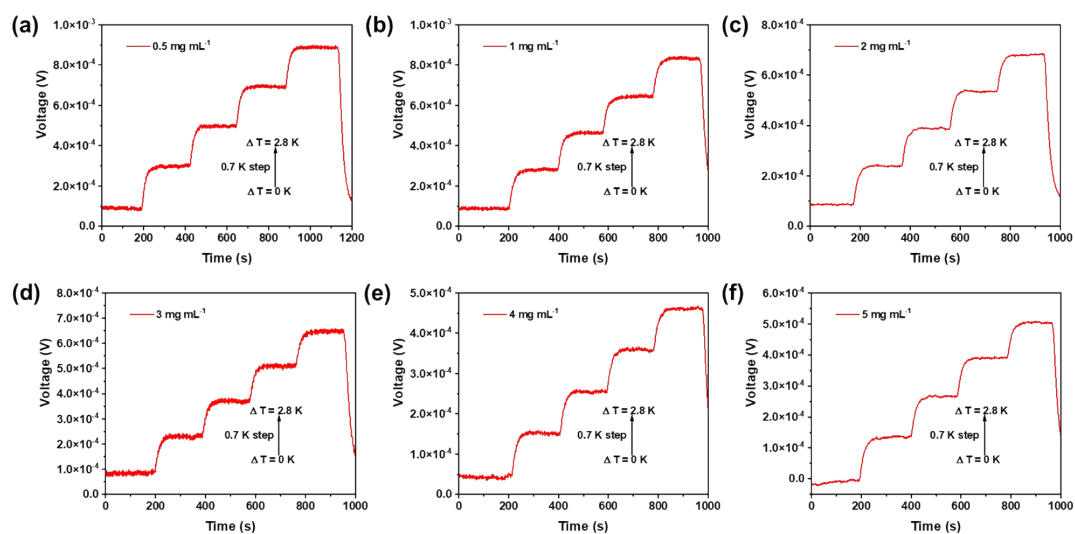


Figure S3. Representative thermal voltage response curves for sequentially doped

CNg4T2-2FT films with distinct *N*-DMBI concentration in *n*-butyl acetate solutions, including (a) 0.5 mg mL⁻¹, (b) 1 mg mL⁻¹, (c) 2 mg mL⁻¹, (d) 3 mg mL⁻¹, (e) 4 mg mL⁻¹, (f) 5 mg mL⁻¹. During the measurement, the temperature difference (ΔT) across the doped polymer films was systematically varied from 0 to 2.8 K with a step of 0.7 K and then back to 0 K.

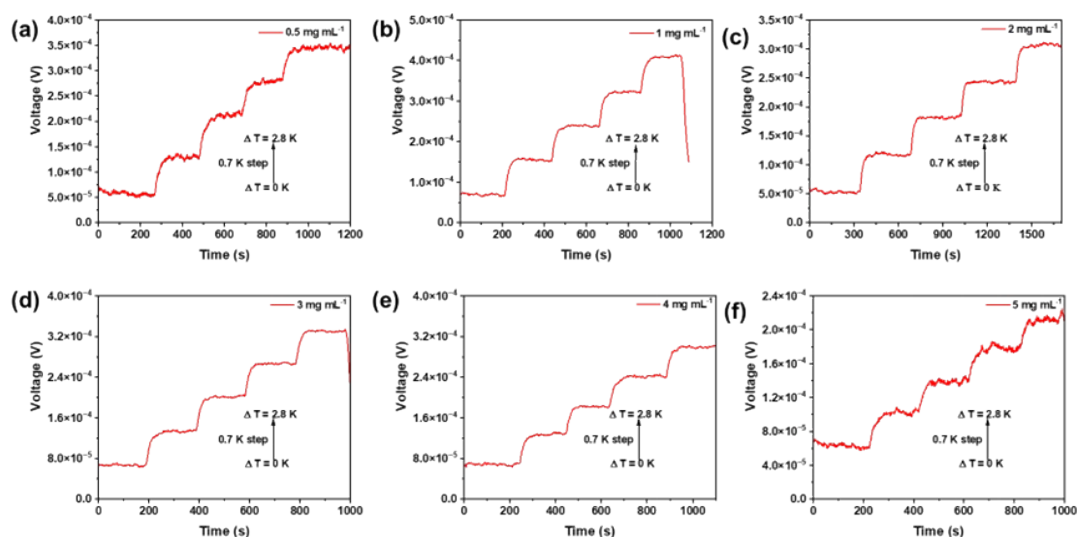


Figure S4. Representative thermal voltage response curves for sequentially doped CNg4T2-CNT2 films with distinct *N*-DMBI concentration in *n*-butyl acetate solutions, including (a) 0.5 mg mL⁻¹, (b) 1 mg mL⁻¹, (c) 2 mg mL⁻¹, (d) 3 mg mL⁻¹, (e) 4 mg mL⁻¹, (f) 5 mg mL⁻¹. During the measurement, the temperature difference (ΔT) across the doped polymer films was systematically varied from 0 to 2.8 K with a step of 0.7 K and then back to 0 K.

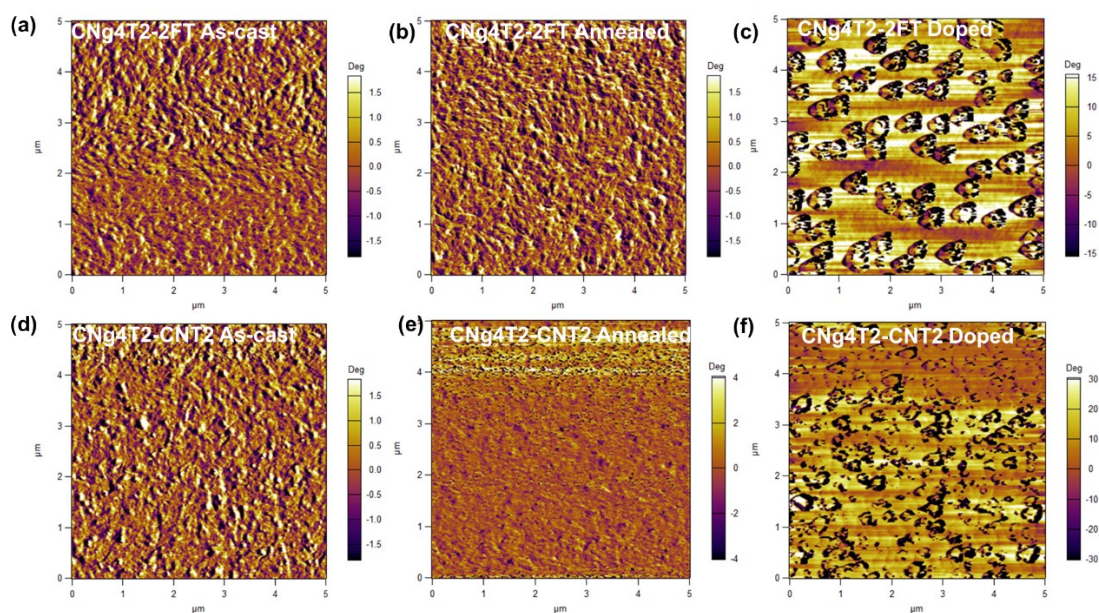


Figure S5. Atomic Force microscope height image of CNg4T2-2FT film: (a) as-cast, (b) annealed, and (c) doped film; Atomic Force microscope height image of CNg4T2-CNT2 film: (d) as-cast, (e) annealed, and (f) doped film.

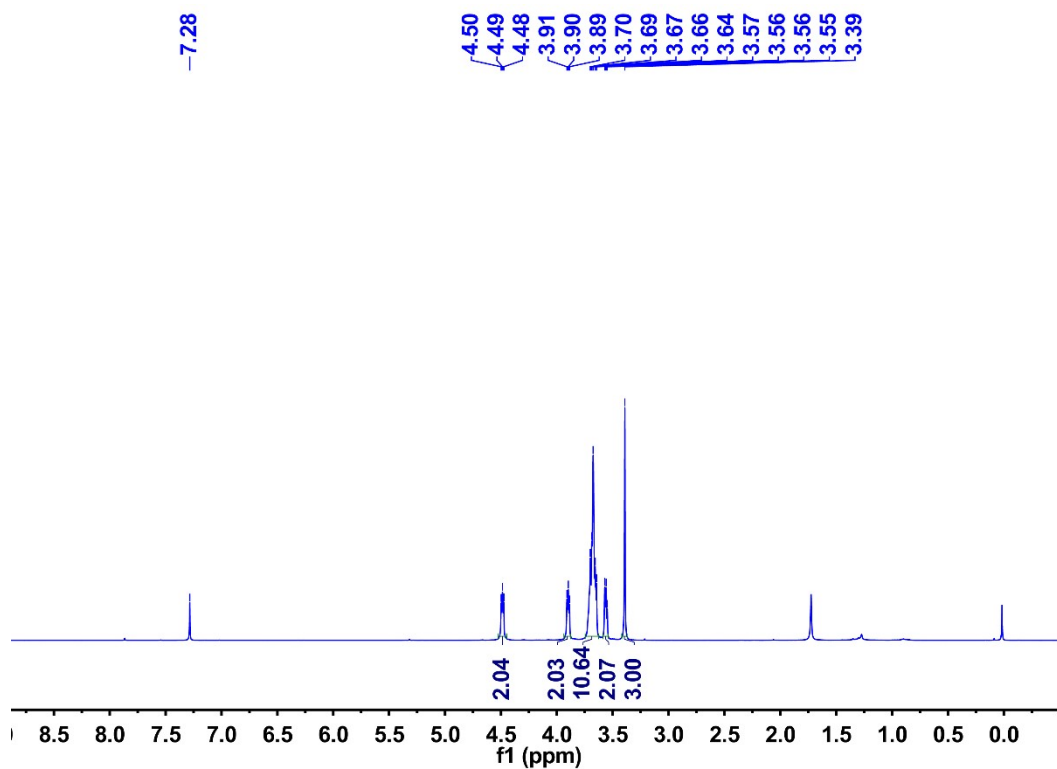


Figure S6. The ^1H NMR spectrum of CNg4T2-2Br.

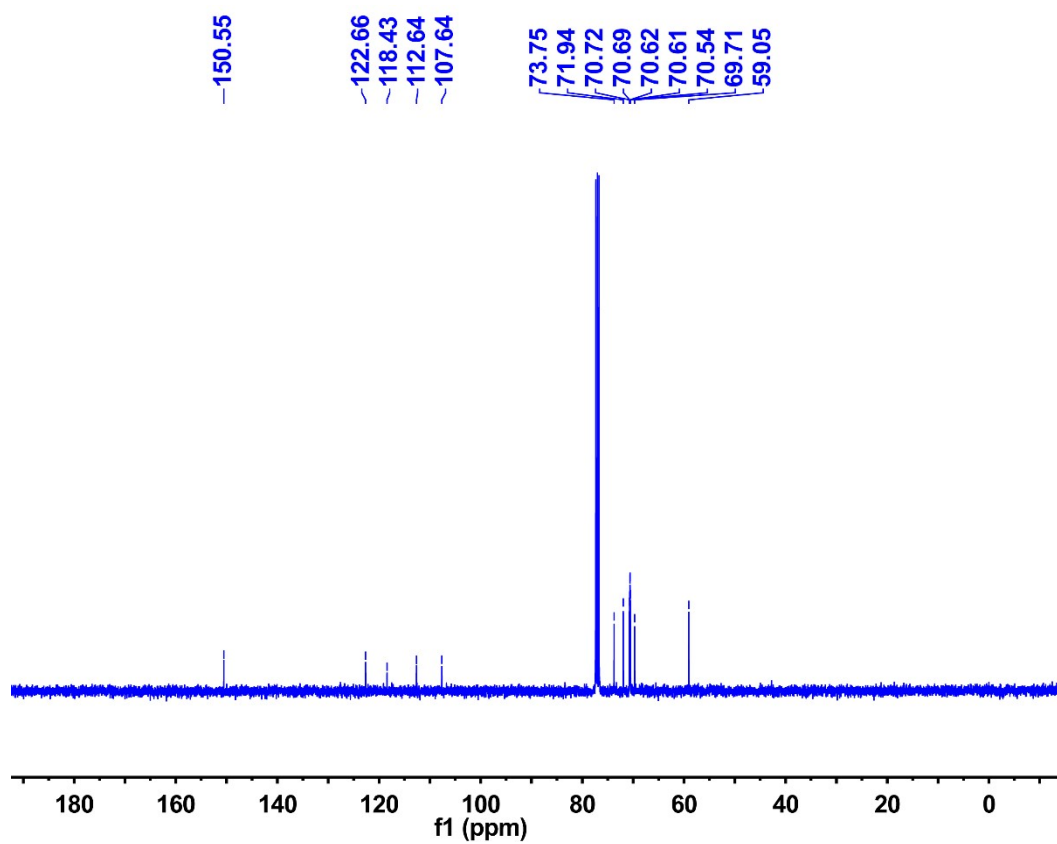


Figure S7. The ^{13}C NMR spectrum of CNg4T2-2Br.

References

1. Y. Wang, Z. Yan, H. Guo, M. A. Uddin, S. Ling, X. Zhou, H. Su, J. Dai, H. Y. Woo and X. Guo, *Angew. Chem. Int. Ed.*, 2017, **56**, 15304-15308.
2. X. Yan, M. Xiong, J.-T. Li, S. Zhang, Z. Ahmad, Y. Lu, Z.-Y. Wang, Z.-F. Yao, J.-Y. Wang, X. Gu and T. Lei, *J. Am. Chem. Soc.*, 2019, **141**, 20215-20221.