

Supporting information for

Chlorinated Phenazine-Based Conjugated Copolymers with Enhanced Open-Circuit Voltage for Polymer Solar Cells

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Experiment details

Materials synthesis

Toluene was distilled from sodium under nitrogen atmosphere using benzophenone as an indicator. All other reagents were used as purchased. 2,3-dichloro-7,8-bis(decyloxy)phenazine,¹ tributyl(thiophen-2-yl)stannane and 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-N-9"-heptadecanyl-carbazole (**M2**) were prepared according to the literature.²

Synthesis of compound **1,4-dibromo-7,8-dichloro-2,3-bis(decyloxy)phenazine**.

A mixture of **2,3-dichloro-7,8-bis(decyloxy)phenazine** (4.5 g, 8 mmol) and N-bromo succinimide (3.2 g, 18 mmol) and dimethylformamide (400ml) was stirred for 48h at room temperature and then poured into brine. It was then extracted with dichloromethane, the two phases were separated, and the water phase was extracted twice with dichloromethane. The combined organic extracts were washed three times with water, dried over sodium sulfate, evaporated, and purified with column chromatography (silica gel, petroleum ether/dichloromethane (5/1) as eluent) to yield 2.3g (40%) of **3** as a greenish solid. ¹H NMR (300 MHz, CDCl₃) δ 8.53 (s, 2H), 4.27 (t, J = 6.6 Hz, 4H), 2.01–1.88 (m, 4H), 1.65–1.51 (m, 4H), 1.34 (m, 24H), 0.90 (t, J = 6.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 155.45, 141.04, 139.87, 135.94, 129.52, 116.28, 75.14, 31.93, 30.37, 29.65, 29.62, 29.48, 29.36, 26.04, 22.70, 14.12. MALDI-TOF (m/z):717.1 [M+H]⁺.

7,8-Dichloro-2,3-bis(decyloxy)-1,4-di(thiophen-2-yl)phenazine

PdCl₂(PPh₃)₂ (21 mg, 0.03 mmol) was added to a solution of compound **1,4-dibromo-7,8-dichloro-2,3-bis(decyloxy)phenazine** (2.16 g, 3 mmol) and tributyl(thiophen-2-yl)stannane (3.3 g, 9.0 mmol) in 60ml THF. The mixture was refluxed in an argon atmosphere for 36h. The reaction was quenched with aqueous NaHCO₃ and extracted with dichloromethane. The two phases were separated, and the water phase was extracted twice with dichloromethane. The combined organic extracts were washed three times with water, dried over sodium sulfate, evaporated, and purified with column chromatography (silica gel, petroleum

ether/dichloromethane (1/1) as eluent) to yield 1.61 g (75%) ^1H NMR (300 MHz, CDCl_3) δ 8.44–8.38 (s, 2H), 8.00 (dd, $J = 7.7, 4.9$ Hz, 2H), 7.65–7.58 (m, 2H), 7.28–7.25 (m, 2H), 4.08 (t, $J = 6.7$ Hz, 4H), 1.88–1.72 (m, 4H), 1.45–1.23 (m, 28H), 0.95–0.85 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 154.45, 140.69, 139.83, 134.57, 133.12, 131.09, 129.69, 127.93, 126.22, 123.69, 74.41, 31.96, 30.39, 29.65, 29.62, 29.50, 29.39, 26.01, 22.73, 14.15. MALDI-TOF (m/z): 724.3 $[\text{M}+\text{H}]^+$

1,4-Bis(5-bromothiophen-2-yl)-7,8-dichloro-2,3-bis(decyloxy)phenazine (M1)

Compound **7,8-dichloro-2,3-bis(decyloxy)-1,4-di(thiophen-2-yl)phenazine** (1.3 g, 1.8 mmol) was dissolved in 100 ml of dichloromethane, and then N-bromosuccinimide (0.96 g, 5.4 mmol) was added in portions. The mixture was stirred at room temperature for 24 h. Then the mixture was poured into brine and extracted twice with dichloromethane. The combined organic phases were dried over sodium sulfate, evaporated. The crude product was purified with column chromatography (silica gel, petroleum ether/dichloromethane (1/1) as eluent) to yield 1.2 g (75%) of **M1** as brown solid. ^1H NMR (300 MHz, CDCl_3) δ 8.45 (s, 2H), 7.98 (d, $J = 4.1$ Hz, 2H), 7.20 (d, $J = 4.1$ Hz, 2H), 4.11 (t, $J = 6.8$ Hz, 4H), 1.93–1.77 (m, 4H), 1.50–1.21 (m, 28H), 0.91 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 154.10, 139.46, 139.26, 135.10, 134.73, 131.33, 129.22, 128.96, 122.51, 116.67, 74.38, 31.95, 30.48, 29.67, 29.63, 29.52, 29.40, 26.05, 22.73, 14.15. MALDI-TOF (m/z): 881.1 $[\text{M}+\text{H}]^+$

Synthesis of PCTCIP

2,7-Bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-N-9''-heptadecanyl-carbazole (**M2**) (0.1973 g, 0.3 mmol), **M1** (0.2651 g, 0.3 mmol), $\text{Pd}(\text{PPh}_3)_4$ (2 mg) and Aliquat 336 (0.1 g, 0.25 mmol) were dissolved in a mixture of toluene (10 ml) and 2 M K_2CO_3 solution in water (2 ml) under argon. The mixture was refluxed with vigorous stirring in the dark for 8 h under an argon atmosphere. After reaction completion, phenylboronic acid (12 mg, 0.10 mmol) was added to the reaction then six hours later, bromobenzene (11 μL , 0.10 mmol) was added and the reaction refluxed overnight to complete the end-capping reaction. After cooling to room temperature, the mixture was poured into methanol. The obtained solid was dissolved in chloroform. The solution was washed with water and dried with anhydrous Na_2SO_4 for 30 min. After most of the solvent was removed, the residue was poured into stirred methanol. The precipitated material was collected by filtration through a funnel. After washing with acetone and hexane each for 12 h in a Soxhlet apparatus to remove oligomers and catalyst residues, the resulting material was dried in vacuum to yield 284 mg (84%). NMR (300 MHz, CDCl_3) δ 8.50 (br, 2H), 8.17 (br, 4H), 7.89 (m, 2H), 7.69 (d, $J = 7.1$ Hz, 2H), 7.60 (br, 2H), 4.72 (br, 1H), 4.22 (br, 4H), 2.47 (br, 2H), 2.00 (m, 6H), 1.76 – 1.04 (m, 46H), 0.85 (t, $J = 6.3$ Hz, 6H), 0.77 (t, $J = 6.3$ Hz, 6H).

General characterization methods

^1H and ^{13}C NMR were recorded using a Bruker-300 or 400 spectrometer operating at 300 or 400 and 101 MHz in deuterated chloroform solution at 298K. Chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane (TMS)

standard. MALDI-TOF mass spectra were performed on an AXIMA CFR MS apparatus (COMPACT). The molecular weights (MWs) and molecular weight distributions of the polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature gel permeation chromatography. 1,2,4- Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 ml min⁻¹ and the calibration was made with a polystyrene standard Easi-Cal PS-1 (PL Ltd). Thermal properties of the polymer were analyzed with a Perkin-Elmer-TGA 7 instrument under nitrogen at a heating rate of 10 °C/min. UV–visible absorption spectra were measured with a Perkin-Elmer Lambda 35 UV–vis spectrometer. CV experiments were performed on an EG&G 283 (Princeton Applied Research) potentiostat/galvanostat system. A platinum working electrode and a Pt wire counter electrode at a scan rate of 50 mV s⁻¹, against an Ag/AgCl reference electrode with a nitrogen-saturated anhydrous solution of 0.1 mol L⁻¹ n-Bu₄NClO₄ in acetonitrile. TEM was performed on a JEOL JEM-1011 transmission electron microscope operated at an acceleration voltage of 100kV.

Solar cell device fabrication and characterization. The solar cell was fabricated with a device structure of glass/indium tin oxide (ITO)/copolymer:PCBM/LiF/Al. A mixture of copolymer and PCBM were dissolved in chlorobenzene and stirred overnight for complete dissolution. A 40 nm-thick PEDOT:PSS (Baytron P AI 4083) layer was spin-coated onto the pre-cleaned ITO substrate and dried at 120°C for 30min in an oven. The ca. 80 nm thick copolymer:PCBM active layer was deposited on the PEDOT:PSS layer via spin-coating from 5mg/ml copolymer:PCBM solution. Finally, a bilayer structure of LiF (0.5nm)/Al (100nm) was thermally deposited atop the active layer in vacuum chamber under a base pressure of about 4×10⁻⁴Pa. the cell active area was 12mm², which was defined by the overlapping area of the ITO and Al electrodes. When THF solvent annealing is used to control phase separation between polymer and PCBM, put the spin coated device inside a Petri dish with saturated THF vapor for a controlled time. Then the cathode is deposited.

The current density-voltage (J-V) characteristic was measured using a computer-controlled Keithley 236 source meter. An oriel 150 W solar simulator with an AM 1.5G filter was used to provide an intensity of 100 mW/cm² for illumination of the photovoltaic cells. The light intensity was determined by a calibrated silicon diode with KG-5 filter. The EQE measurement was performed under short-circuit conditions with a lock-in amplifier (SR830, Stanford Research System) at a chopping frequency of 280 Hz during illumination with a monochromatic light from a Xenon lamp. About 8 devices were made for each condition and tested.

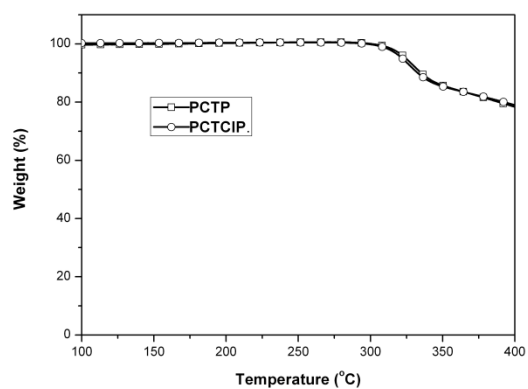


Fig. S1. TGA curves of the copolymer **PCTP** and **PCTCIP** with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in N_2

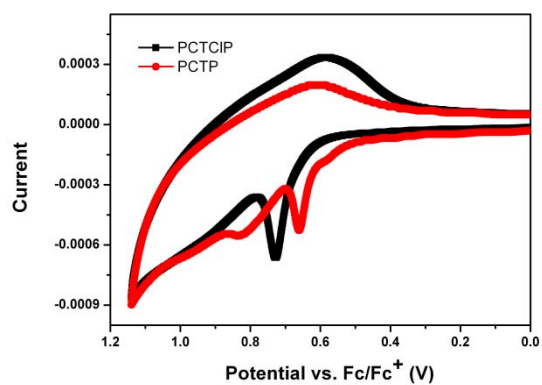


Fig. S2 Cyclic voltammograms of the films of **PCTP** and **PCTCIP**.

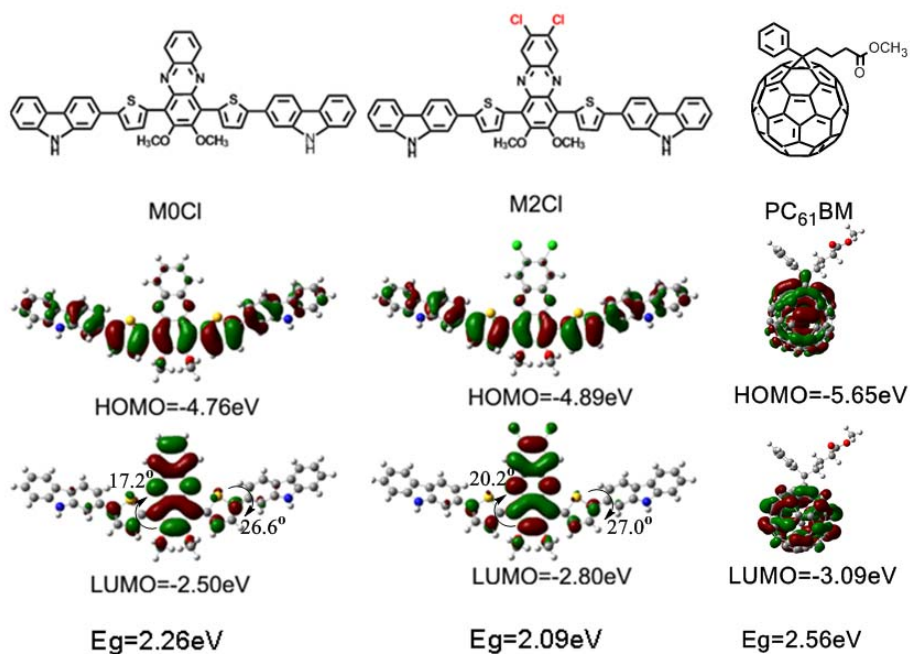


Fig. S3. Calculated HOMO and LUMO distributions for **M0Cl**, **M2Cl** and PC₆₁BM.

Molecular geometries of **M0Cl**, **M2Cl** and PC₆₁BM were optimized using density functional theory at B3LYP/6-31G(d) level.³ To simplify the calculation, the alkoxy groups of phenazine are replaced by methoxy groups and alkyl groups on carbazole are replaced by methyl groups. Frequency calculations were performed at B3LYP/6-31G(d) level. The isodensity coefficient used to illustrate the HOMO/LUMO is 0.02. All calculations were carried out using the Gaussian 03 suite of programs.³

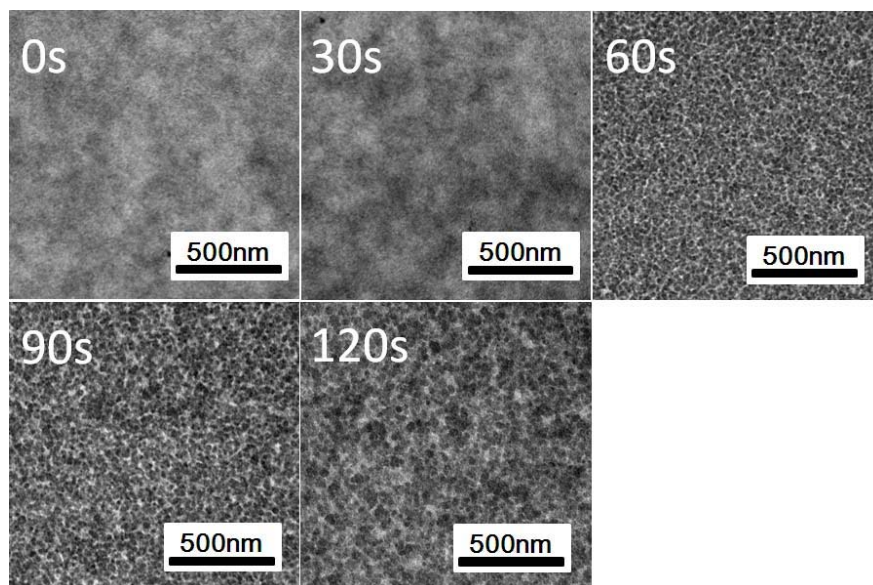


Fig S4. TEM images of PCTCIP/PC₇₁BM composite films after THF vapor annealing with different time

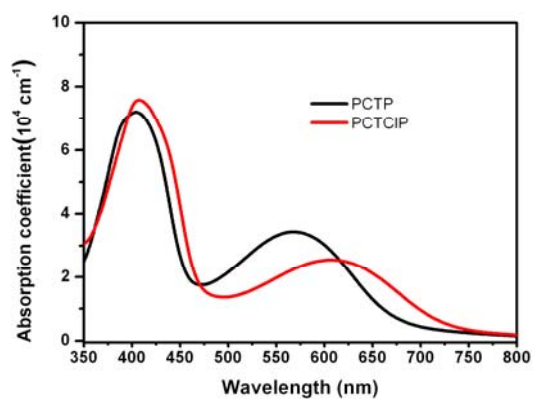


Fig S5. UV-vis absorption coefficient of the copolymers films.

Table S1 Device performance of the copolymer/PC₇₁BM photovoltaic devices after solvent vapor annealing (SVA) treatment in THF vapor.

Active layer	SVA (s)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE _{max} (PCE _{average}) (%)	Thickness (nm)
PCTP/ PC₇₁BM (1/3)	0	0.87	7.48	0.39	2.54(2.51)	80
	30	0.85	7.66	0.39	2.59(2.54)	80
	60	0.81	7.68	0.56	3.49(3.46)	80
	90	0.81	7.47	0.53	3.25(3.20)	80
	120	0.81	7.18	0.54	3.16(3.12)	80
PCTCIP/ PC₇₁BM (1/3)	0	0.92	7.61	0.41	2.87(2.85)	79
	30	0.91	7.50	0.42	2.87(2.83)	79
	60	0.87	8.06	0.58	4.06(4.01)	79
	90	0.87	8.06	0.55	3.88(3.85)	79
	120	0.88	6.70	0.58	3.44(3.42)	79

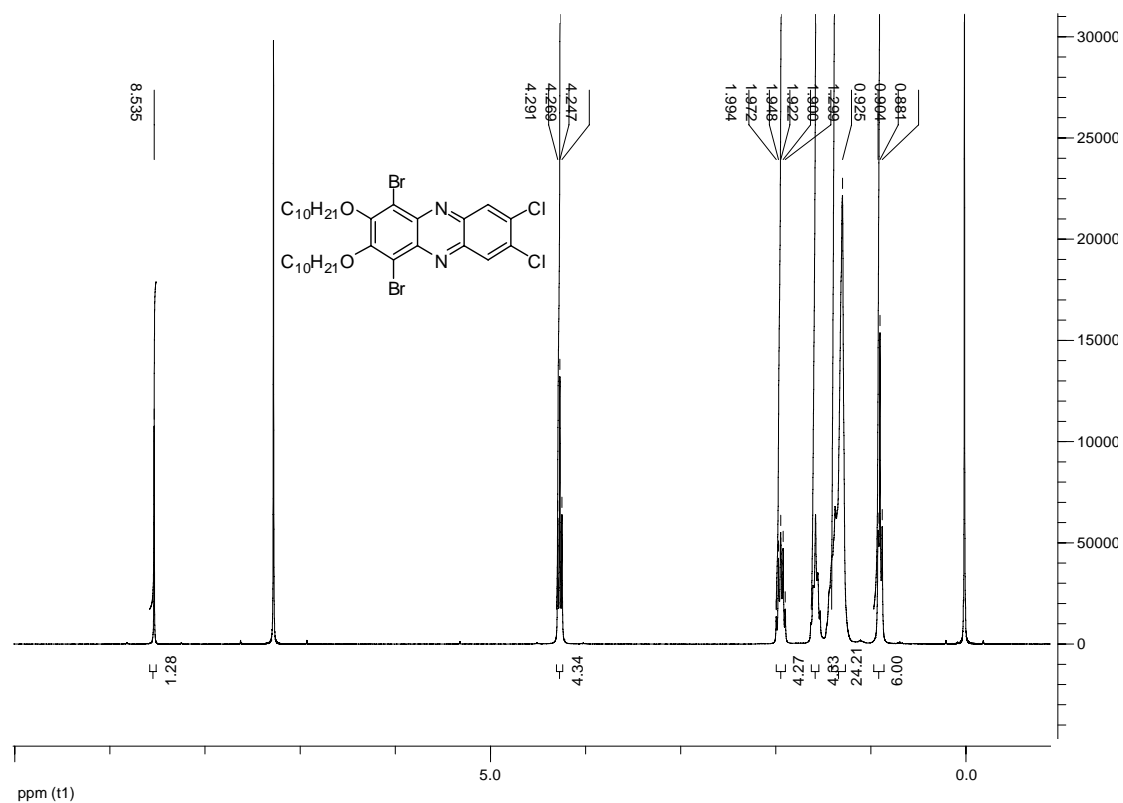


Fig. S6. ^1H NMR of compound **1,4-dibromo-7,8-dichloro-2,3-bis(decyloxy)phenazine** in CDCl_3

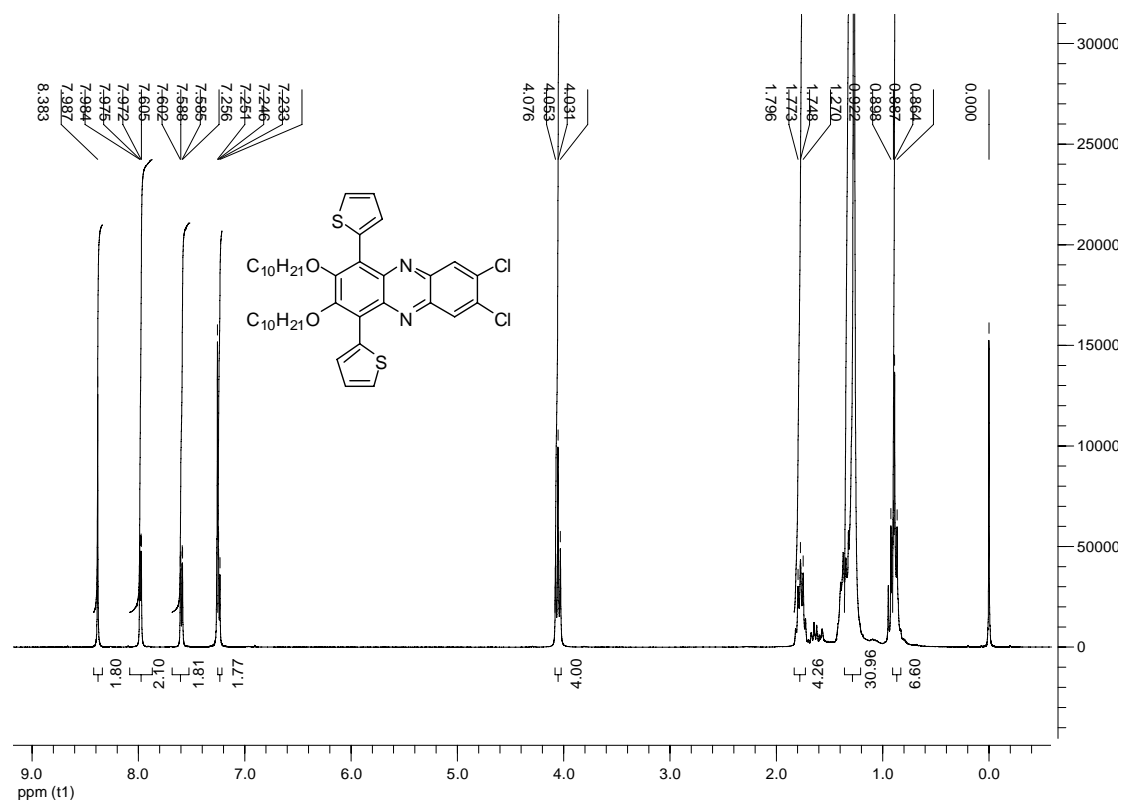


Fig. S7. ^1H NMR of compound **7,8-dichloro-2,3-bis(decyloxy)-1,4-di(thiophen-2-yl)phenazine** in CDCl_3

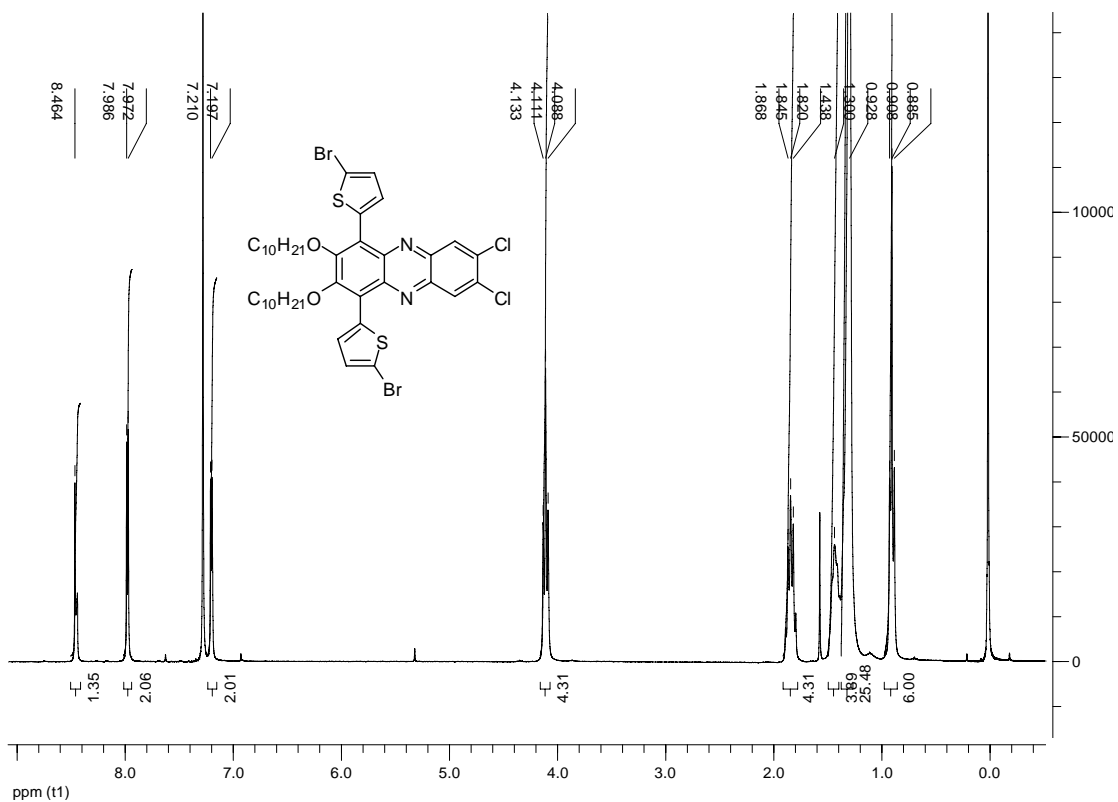


Fig. S8. 1H NMR of compound M1 in $CDCl_3$

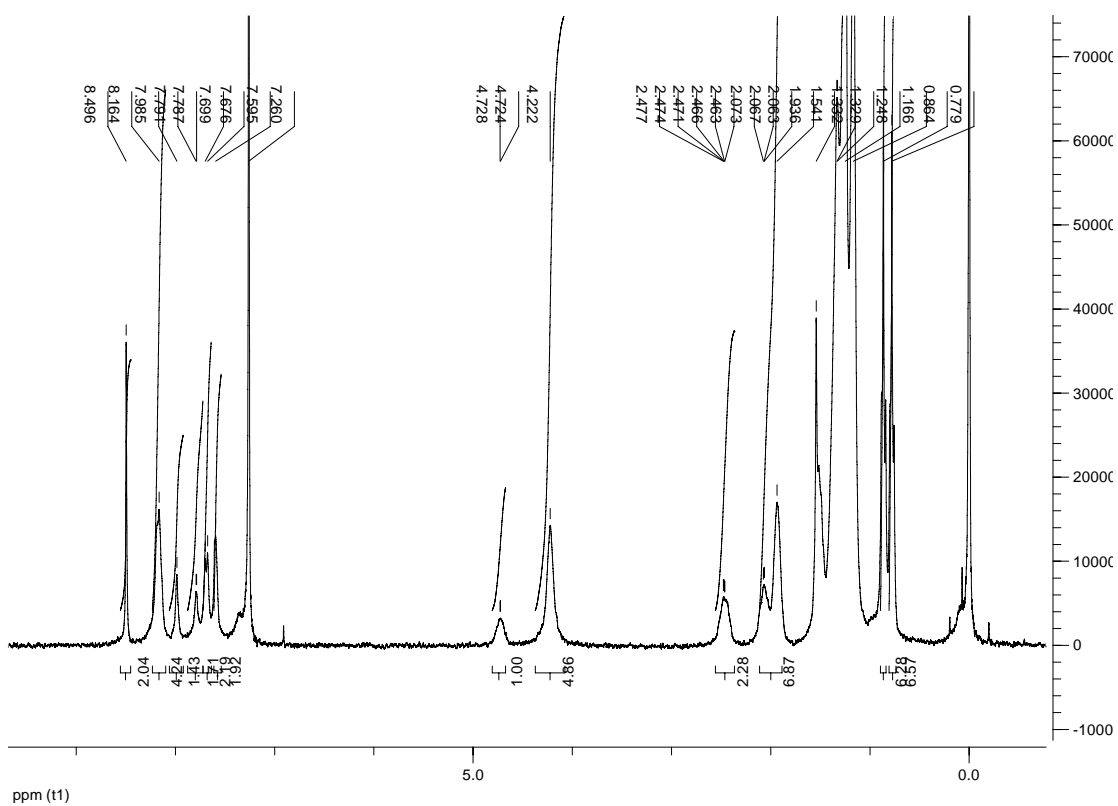


Fig. S9. 1H NMR of polymer PCTCIP in $CDCl_3$

Reference:

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