Supporting Information:

Soluble Ladder Conjugated Polymer Composed of Perylenebisimides and Thieno[3,2-b]thiophene (LCPT): a Highly Efficient Synthesis via Photocyclization with the Sunlight

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1 Material and methods

2,5-Bis(trimethylstannyl)thieno[3,2-b]thiophene (**2**) was synthesized by an improved literature method.[S1] 1-Bromoperylene bisimides (**1**) and 1,7-dibromoperylene bisimides (**5**) were synthesized according to Scheme S1. *N,N'*-bis(12-tricosanyl)perylene bisimides (**6**) was synthesized by a literature method,[S2] while the reagent tricosan-12-amine was synthesized with a new method, as shown in Scheme S2. All other reactants were purchased from commercial sources. NMR spectra were measured with a Bruker spectrometer using TMS as reference.

Cyclic voltammetry (CV) was performed with a standard commercial electrochemical analyzer in a three electrode single-component cell under argon with a scan rate of 100 mV/s. Working electrode: glassy carbon with the area 7 mm^2; reference electrode: Ag/AgCl; auxiliary electrode: Pt disk; supporting electrolyte: tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.05M in electrochemical tests); internal standard: ferrocene (Fc). For polymer SCPT and LCPT, CV was conducted with glassy carbon electrode coated with thin SCPT or LCPT film in DMF solution; polymer film for CV test was made by the following procedure: 1) The carbon electrode was dipped in the 10^{-4} M SCPT or LCPT solution in chloroform, and was took out immediately, 2) The carbon electrode was kept in the air for several minutes, making the solvent evaporate, 3) The above dipping and airing was repeated for seven times; the thickness of above SCPT and LCPT film is about 100nm and 170nm respectively which is determined by a 3D surface profiler. For **3** and **4**, CV was conducted in CH_2Cl_2 solution of **3** or **4**.

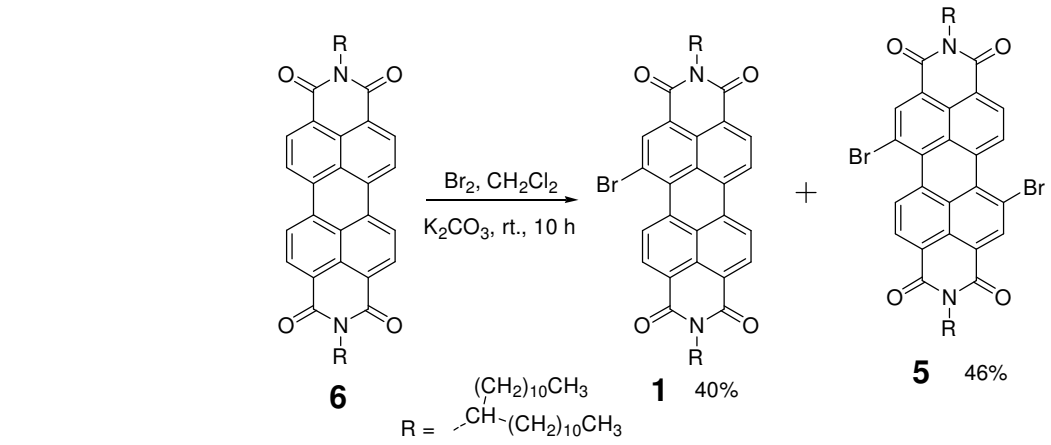
The quantum chemical calculations were performed with the Gaussian03 package.[S3] Absorption spectra were determined on a HP-8453 UV-Vis spectrophotometer. Fluorescence spectra were measured on a JASCO FP-6500 fluorescence. The fluorescence quantunthm yields were determined with Rhodamine 6G as reference.[S4]

S1: M. Sato, A. Asami, G. Maruyama, M. Kosuge, J. Nakayama, S. Kumakura, T. Fujihara, K. Unoura, *J. Organomet. Chem.* **2002**, *654*, 56.

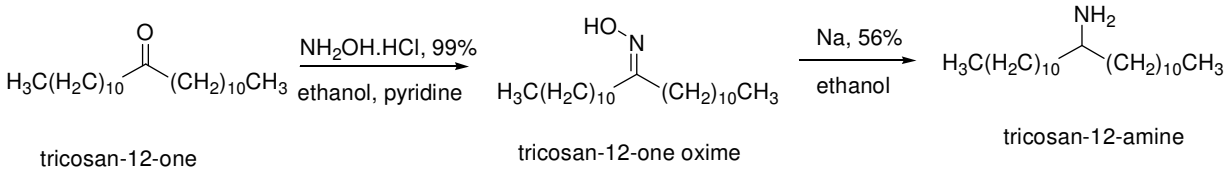
S2: M. J. Tauber, R. F. Kelley, J. M. Giaimo, B. Rybtchinski, M. R. Wasielewski, *J. Am. Chem. Soc.* **2006**, *128*, 1782.

S3: M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, T. Jr. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J.A. Pople. Gaussian 03, revision E.01; Gaussian, Inc.: Wallingford CT, **2004**.

S4: M. Fischer, J. Georges, *Chem. Phy. Lett.* **1996**, *260*, 115.



Scheme S1. Synthesis of **1** and **5**



Scheme S2. Synthesis of tricosan-12-amine

2 Synthesis of intermediates and target compounds

Synthesis of tricosan-12-amine

A mixture of tricosan-12-one (4.9 g, 14.5 mmol), hydroxyamine hydrochloride (2.9 g, 41.7 mmol), 25 mL pyridine, and 50 mL ethanol was stirred at reflux for 3 h. After distillation, the residue was washed with water, and extracted with hexane. After removal of solvent in organic phase, tricosan-12-one oxime was obtained as white solid (5.1g, 99%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 6H), 1.20-1.40 (m, 32H), 1.47 (m, 4H), 2.16 (t, 4H), 2.32 (t, 4H), 7.0-8.0 ppm (br. s, 1H).

A mixture of tricosan-12-one oxime (1.5 g, 4.2 mmol) and 40 mL ethanol was heated to reflux. Then sodium (4.3 g, 23 mmol) was added to the mixture gradually in 2 h. The crude product was recrystallized in mixed solvent (ethanol: water = 5:1, v/v). Tricosan-12-amine (803 mg, 56%) was obtained as white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 6H), 1.11 (s, 2H), 1.20-1.50 (m, 40H), 2.68 ppm (s, 1H).

Synthesis of *N,N′*-bis(12-tricosanyl)perylene bisimides (6)

A mixture of tricosan-12-amine (1.5 g, 4.4 mmol), perylene-3,4,9,10-tetracarboxylic dianhydride (723 mg, 1.8 mmol), and imidazole (5.5g) was stirred at 180^{o}C under Ar gas for 4 h. After purification through silica gel column chromatography, compound **6** (1.85g, 97%) was obtained as a red solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.60-1.40 (m, 84H), 1.86 (m, 4H), 2.24 (m, 4H), 5.19 (m, 2H), 8.56-8.76 ppm (m, 8H).

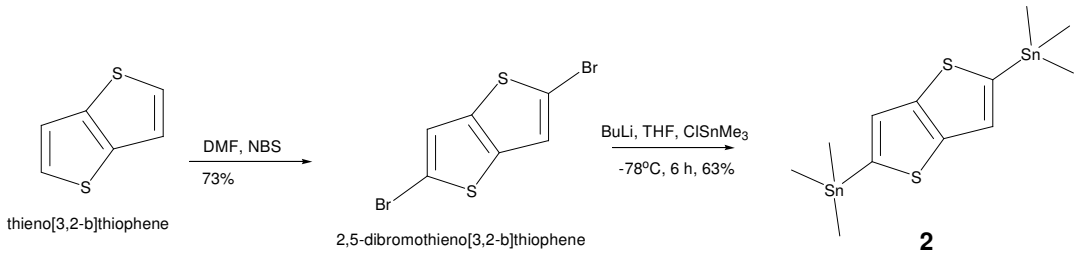
Synthesis of 1 and 5

As shown in Scheme S1, a mixture of compound **6** (3.0 g, 2.9 mmol), K_2CO_3 (10.0 g, 72.5 mmol), 45 mL CH_2Cl_2 and Br_2 (9mL,176.5 mmol) was stirred at room temperature for 10 h. The excess bromine was removed by adding aqueous Na_2SO_3. Then, the crude product was purified through silica gel column chromatography with mixture of dichloromethane and hexane as eluent.

The first band was collected, and after removal of the solvent, compound **1** (1.29 g, 40%) was yielded as a red solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (m, 12H), 1.10-1.60 (m, 72H), 1.85 (m, 4H), 2.26 (m, 4H), 5.19 (m, 2H), 8.62 (d, 2H), 8.70 (m, 3H), 8.92 (m, 1H), 9.79 ppm (d, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 27.0, 29.3, 29.7, 31.9, 32.3, 120.9, 122.9, 123.4, 123.7, 124.0, 127.0, 128.1, 128.7, 129.0, 130.2, 130.7, 131.5, 133.5, 133.8, 138.8, 139.5, 162.4, 163.3, 163.6, 164.3 ppm. MALDI-TOF-MS: Calcd for $C_{70}H_{101}N_2O_4Br$ 1112.6945, found: 1112.7040 (M^+).

The second band was collected, and after removal of the solvent, compound **5** (1.59 g, 46%) was yielded as a red solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (m, 12H), 1.10-1.60 (m, 72H), 1.84 (m, 4H), 2.23 (m, 4H), 5.17 (m, 2H), 8.68 (m, 2H), 8.90 (d, 2H), 9.49 ppm (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 27.0, 29.3, 29.6, 31.9, 32.3, 120.8, 123.0, 127.2, 128.1, 128.5, 129.3, 129.8, 130.5, 132.8, 137.8, 138.5, 162.5ppm. MALDI-TOF-MS: Calcd for $C_{70}H_{100}N_2O_4Br_2$ 1190.6050, found: 1190.6077 (M^+).

Synthesis of 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene (2)



thieno[3,2-b]thiophene

2,5-dibromothieno[3,2-b]thiophene

2

NBS (3.58g, 20.1 mmol, dissolved in 30 mL DMF) was added to a 30 mL DMF solution of thieno[3,2-b]thiophene (1.41g, 10.1 mmol) in a half hour at 0 ^{o}C with stirring. Then the mixture was stirred continued for 3h at 0 ^{o}C and overnight at room temperature. Add the water to the reaction mixture, and the crude product precipitated. After the crude product was recrystallized in mixed solvent (ethanol: water = 5:1, v/v), 2,5-dibromothieno[3,2-b]thiophene (3.0 g, 73%) was obtained as a colorless crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.17 ppm (s, 2H). HRMS: Calcd for $C_6H_2S_2Br_2$ 295.7965, found: 295.7971 (EI, M^+).

BuLi (4.8 mL, dissolved in hexane, 11.1 mmol) was added to the mixture of 2,5-dibromothieno[3,2-b]thiophene (1.5 g, 5.0 mmol) and 50 mL THF at -78 ^{o}C. Above mixture was stirred for 2 h, and then, trimethyltinchloride (2.2 g, 11.1 mmol, dissolved in 20 mL THF) was added gradually. The reaction was continued for another 4 h. After the crude product was recrystallized in ethanol, Compound **2** (1.47 g, 63%) was obtained as a white crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.39 (s, 18H), 7.26 (s, 2H).

Synthesis of 3

A mixture of compound **8** (108 mg, 0.097mmol), compound **2** (19.5 mg, 0.042mmol), 1.6 mg $Pd(PPh_3)_4$, and 6 mL dry toluene was stirred at 90 ^{o}C for 6 h. After purified through silica gel column chromatography, compound **3** was obtained as black solid (91mg, 98%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.80-0.89 (m, 24H), 1.10-1.60 (m, 144H), 1.85 (m, 8H), 2.26 (m, 8H), 5.19 (m, 4H), 7.58 (s, 2H), 8.36 (m, 4H), 8.64-8.81 ppm (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 14.2, 14.3, 22.8, 27.1, 29.4, 29.5, 29.7, 29.8, 32.0, 32.5, 119.9, 123.0, 123.9, 127.6, 128.2, 129.2, 129.3, 130.1, 133.3, 134.1, 134.3, 135.1, 141.5, 147.2, 163.7, 164.4 ppm. MALDI-TOF-MS: Calcd for $C_{146}H_{204}N_4O_8S_2Na$ 2228.5018, found: 2228.5164 ($[M+Na]^+$).

Synthesis of 4

A mixture of compound **3** (36 mg, 0.016mmol), 20 mL toluene and 4 mg I_2 was illuminated by sunlight at reflux for 1 h. After distillation, compound **4** was obtained as red solid (36mg, 100%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.6-3.0 (m, 184H), 5.09 (m, 2H), 5.54 (m, 1H), 5.72 (m, 1H), 8.55-9.20 (m, 10H), 10.34 ppm (br, s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 14.2, 22.8, 27.7, 29.5, 29.6, 29.9, 30.0, 30.2, 32.1, 33.0, 122.9, 123.3, 123.4, 123.7, 124.6, 125.1, 125.4, 126.6, 127.1, 128.7, 132.3, 135.1, 142.5, 163.4, 163.8, 164.8 ppm. MALDI-TOF-MS: Calcd for $C_{146}H_{200}N_4O_8S_2$ 2201.4808, found: 2201.4775 (M^+).

Synthesis of polymer SCPT

A mixture of compound **5** (1.18 g, 0.99 mmol), compound **2** (460 mg, 0.99 mmol), 25 mL dry toluene, and $Pd(PPh_3)_4$ (30 mg) was stirred at 90 °C for 72 h. Then 150 mg end capping reagent **1** and $Pd(PPh_3)_4$ (13 mg) was added to the mixture, and the reaction was continued for another 48 h. The reaction mixture was added to the hexane, filtering, and the filter cake was added to the hexane again. Finally after filtering, polymer SCPT was yielded as black solid (1.0 g, 86%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.8-1.0 (m, 12H), 1.2-1.6 (m, 72H), 1.85 (br. s, 4H), 2.26 (br. s, 4H), 5.19 (br. s, 2H), 7.4-7.8 (m, 2H), 8.3-8.9 ppm (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 22.8, 27.2, 29.5, 29.8, 31.8, 32.1, 32.6, 120.5, 122.7, 123.3, 128.6, 19.5, 130.4, 133.1, 133.3, 134.5, 141.8, 147.2, 163.6, 164.6 ppm.

Synthesis of polymer LCPT

A mixture of 600 mg polymer SCPT**,** 150 mL toluene, and 30 mg I_2 was illuminated by sunlight under reflux for 16 h. Then the mixture was added to 750 mL methanol. After filtration polymer LCPT was yielded as dark solid (599 mg, 100%). ^{1}H-NMR (400 MHz, $C_6D_4Cl_2$): δ = 0-4.2 (m, 92H), 5.5-7.0 (m, 2H), 8.0-11.4 ppm (m, 4H).

3 Time-dependent UV-vis absorption changes for compound 3 and SCPT

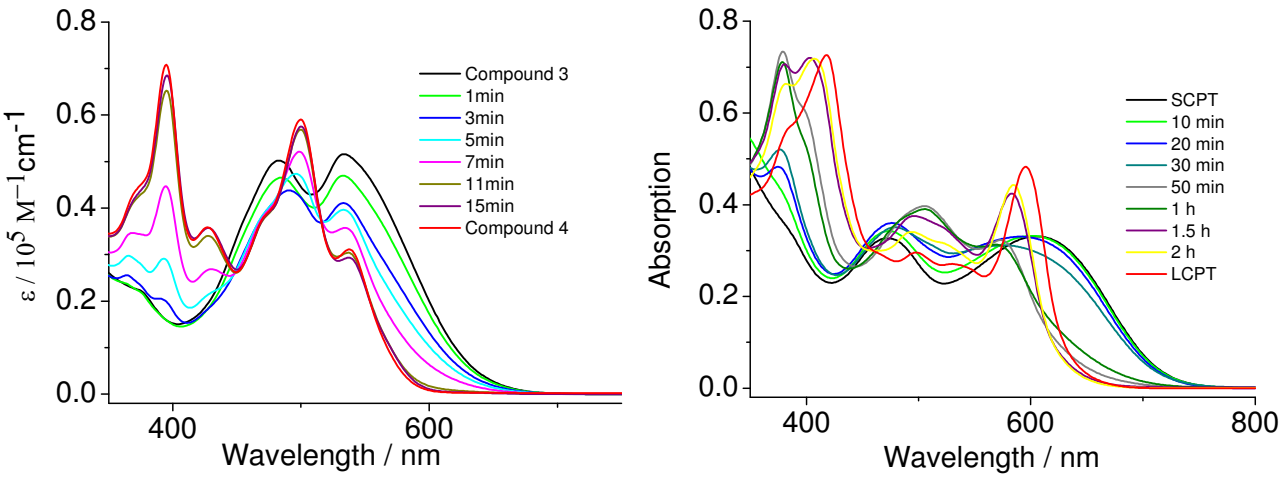
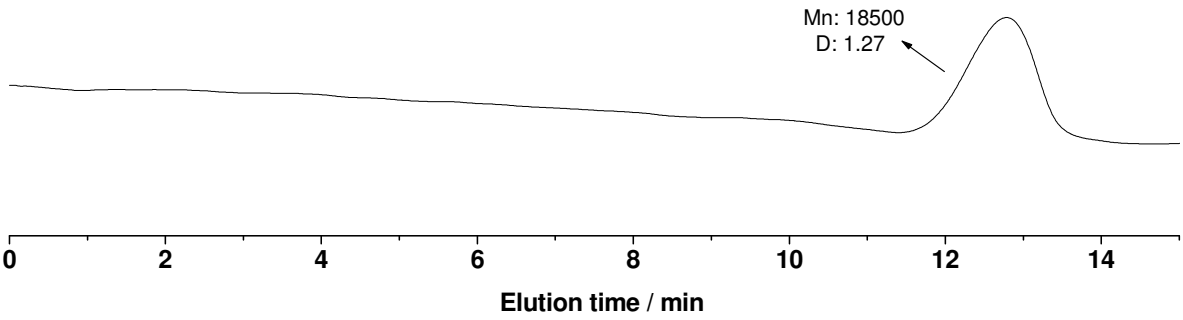


Figure S1 Time-dependent absorption changes for **3** (left) and SCPT (right) in toluene

The photocyclization of **3** or SCPT was done with the concentration of 1.1mg/mL in toluene at reflux in presence of 0.2mg/L I_2 and sunlight; took samples at desired time; the absorption test was done with dilute toluene solution 10^{-5} M (calculated by **3** or monomer) and the absorption of I_2 was eliminated by subtracting the absorption of the other toluene solution of I_2 which underwent the same irradiating and heating as photocyclization of **3** or SCPT.

4 GPC spectrum of SCPT



Mobile phase: THF, polystyrene standards.

Figure S2. GPC spectrum of SCPT

5 DSC curves of SCPT and LCPT

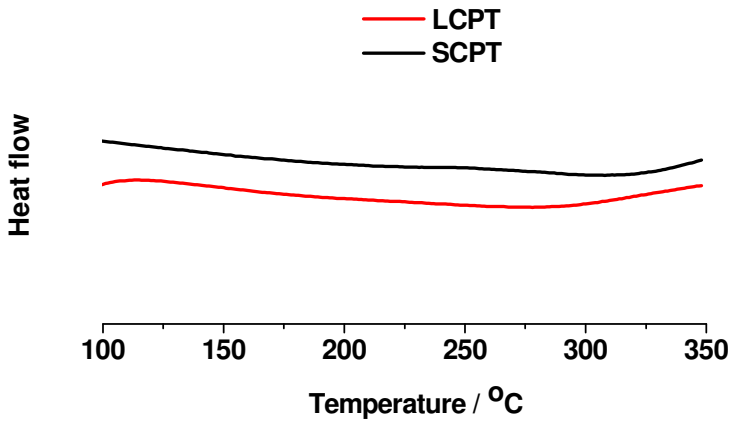
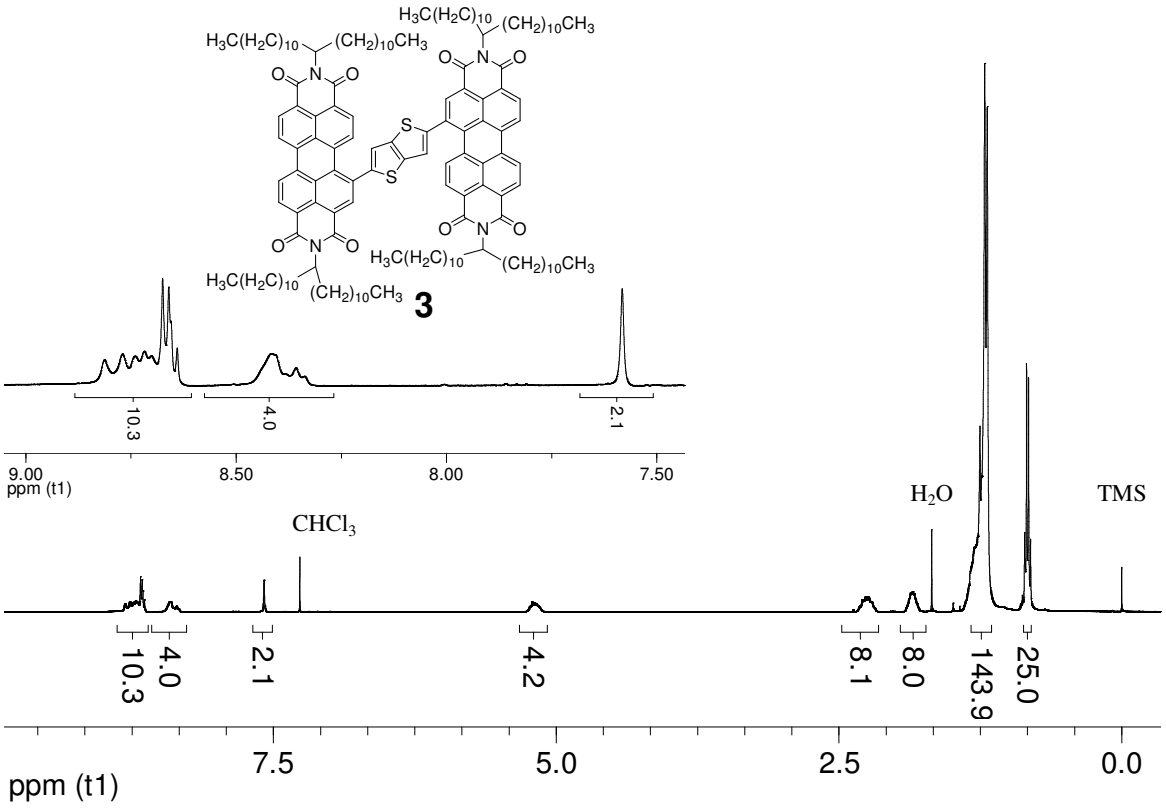


Figure S3. DSC curves of SCPT and LCPT (The second heating scans, 10 $^{o}Cmin^{-1}$)

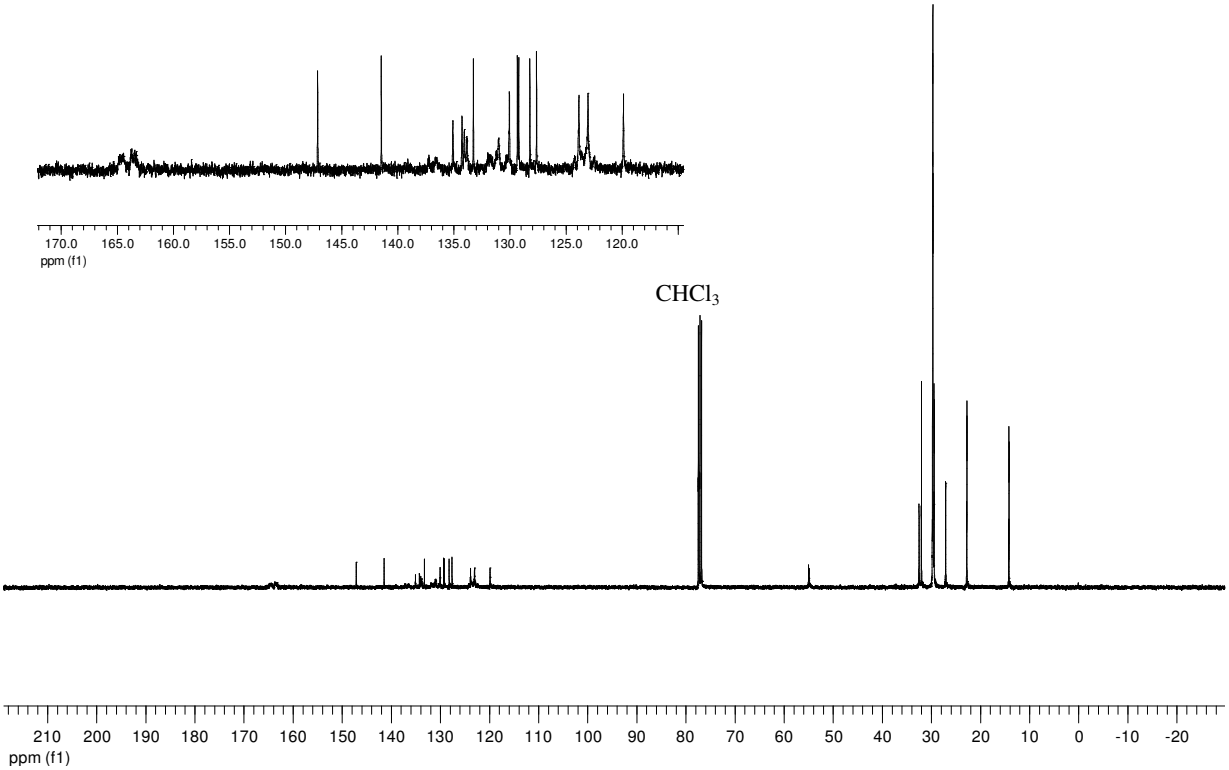
6 Copy of NMR spectrum

6.1 ^{1}H ^{13}C NMR spectrum of 3

^{1}H NMR (400 MHz) spectrum of **3** in $CDCl_3$ and its enlarged low-field section (inserted figure)

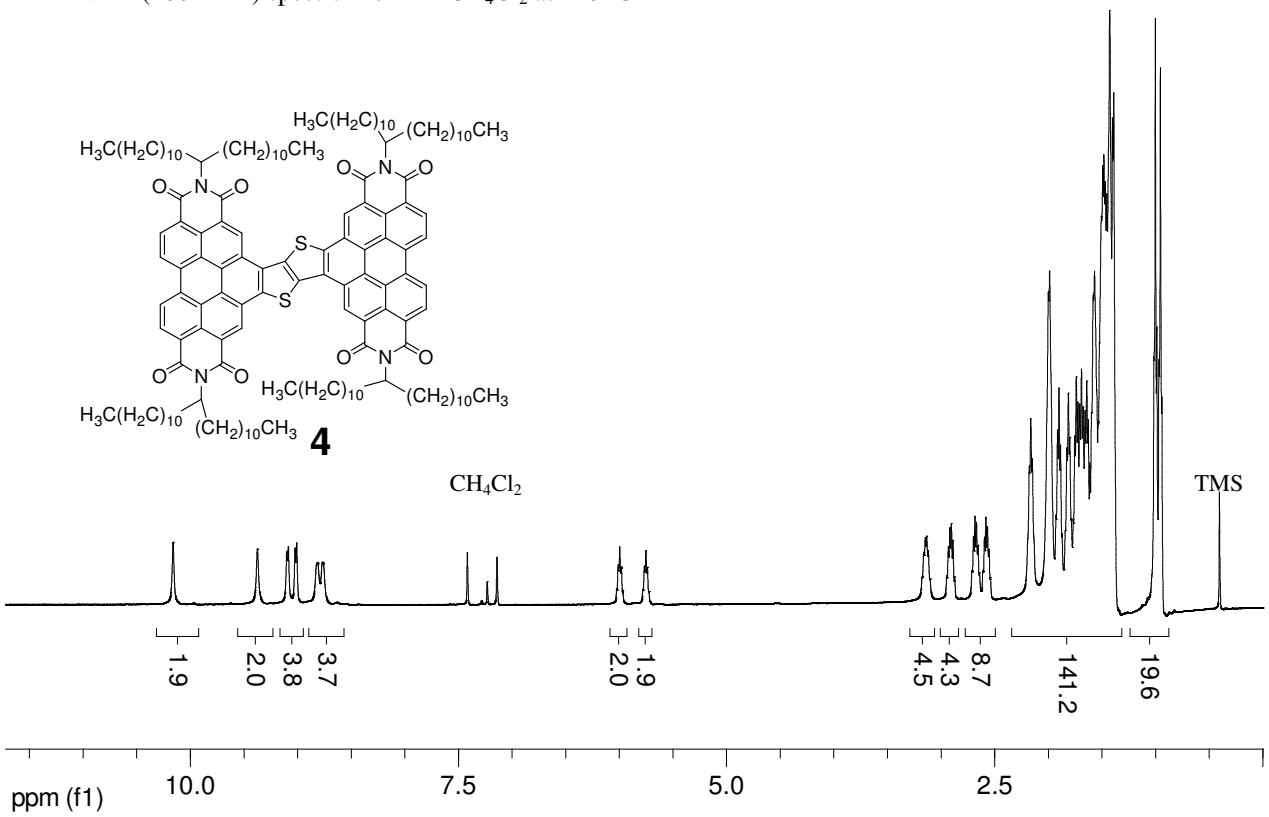


^{13}C NMR (100 MHz) spectrum of **3** in $CDCl_3$ and its enlarged low-field section (inserted figure)

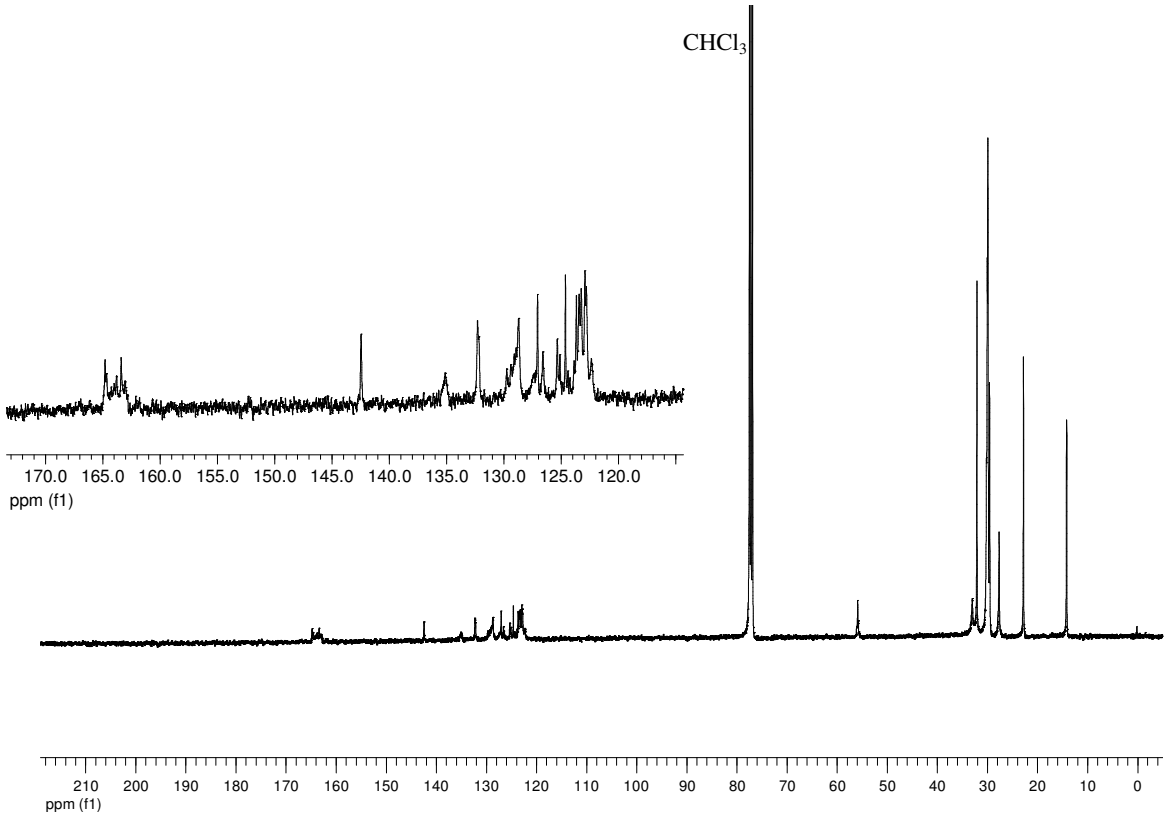


6.2 ^{1}H ^{13}C NMR spectrum of 4

^{1}H NMR (400 MHz) spectrum of **4** in CD_4Cl_2 at 120 °C

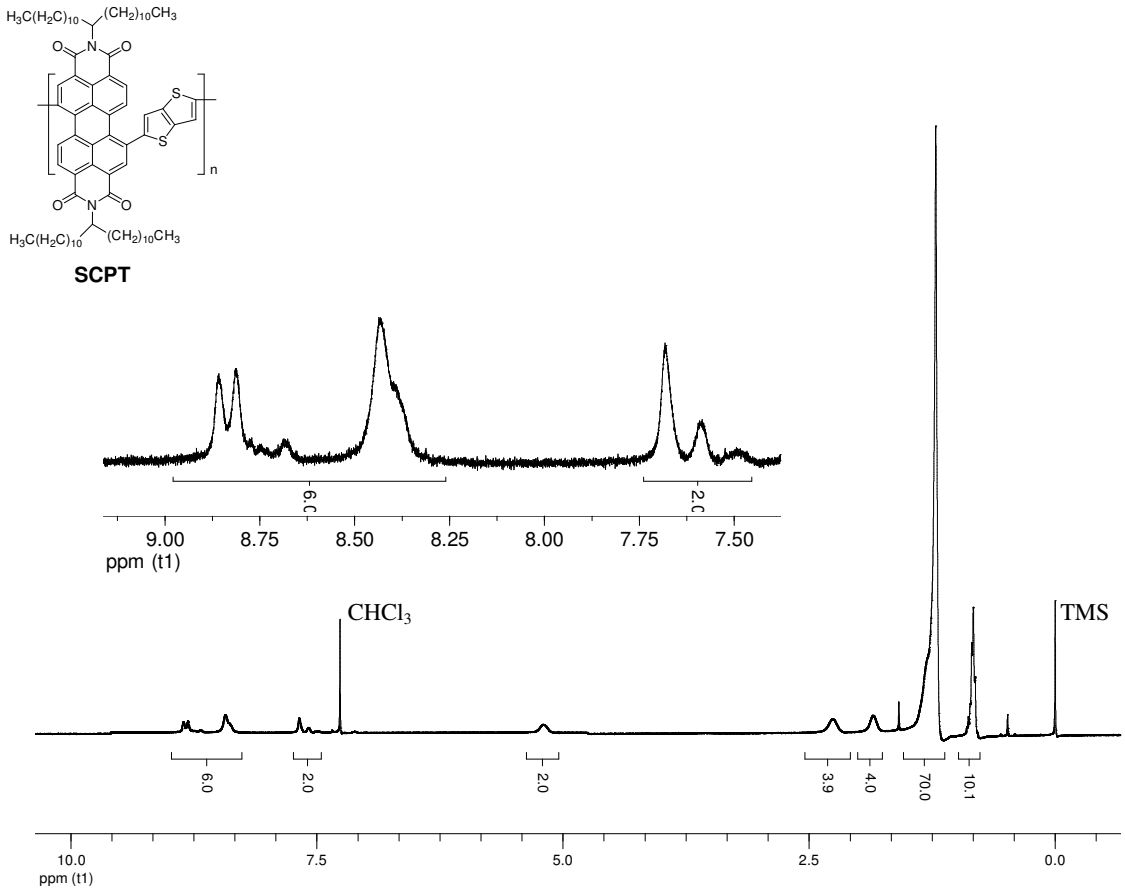


^{13}C NMR (100 MHz) spectrum of **4** in $CDCl_3$ and its enlarged low-field section (inserted figure)

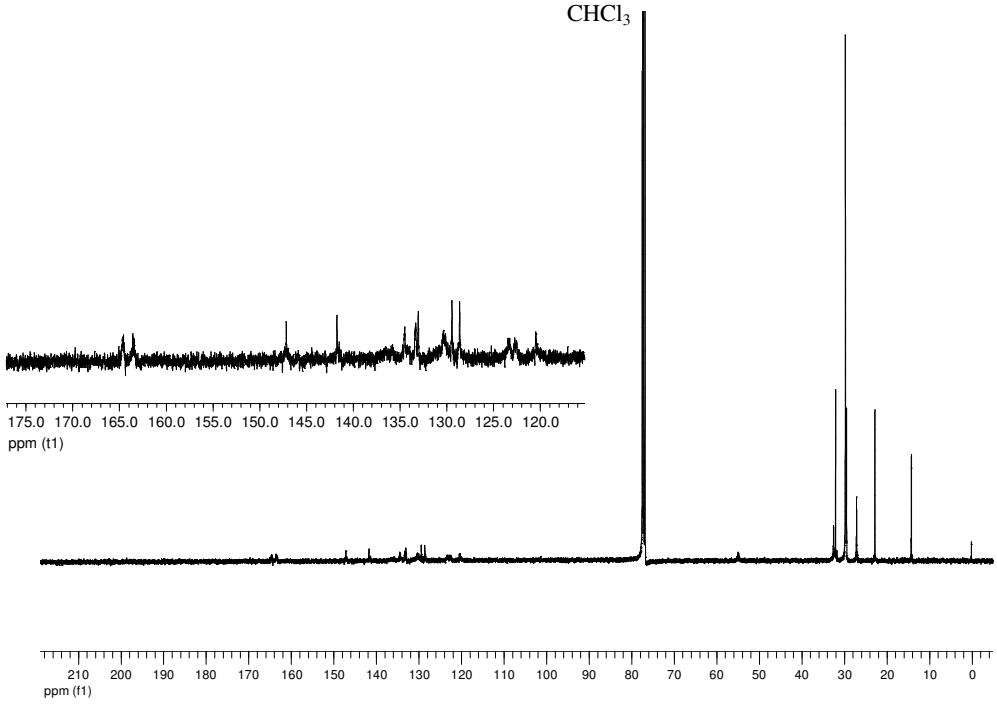


6.3 ^{1}H ^{13}C NMR spectrum of SCPT

^{1}H NMR (400 MHz) spectrum of SCPT in $CDCl_3$ and its enlarged low-field section (inserted figure)



^{13}C NMR (100 MHz) spectrum of SCPT in $CDCl_3$ and its enlarged low-field section (inserted figure)



6.4 ^{1}H NMR spectrum of LCPT

^{1}H NMR (400 MHz) spectrum of LCPT in $C_6D_4Cl_2$ at 120 ^{o}C