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Supplementary Information for

A Reversibly Mechanochromic Conjugated Polymer

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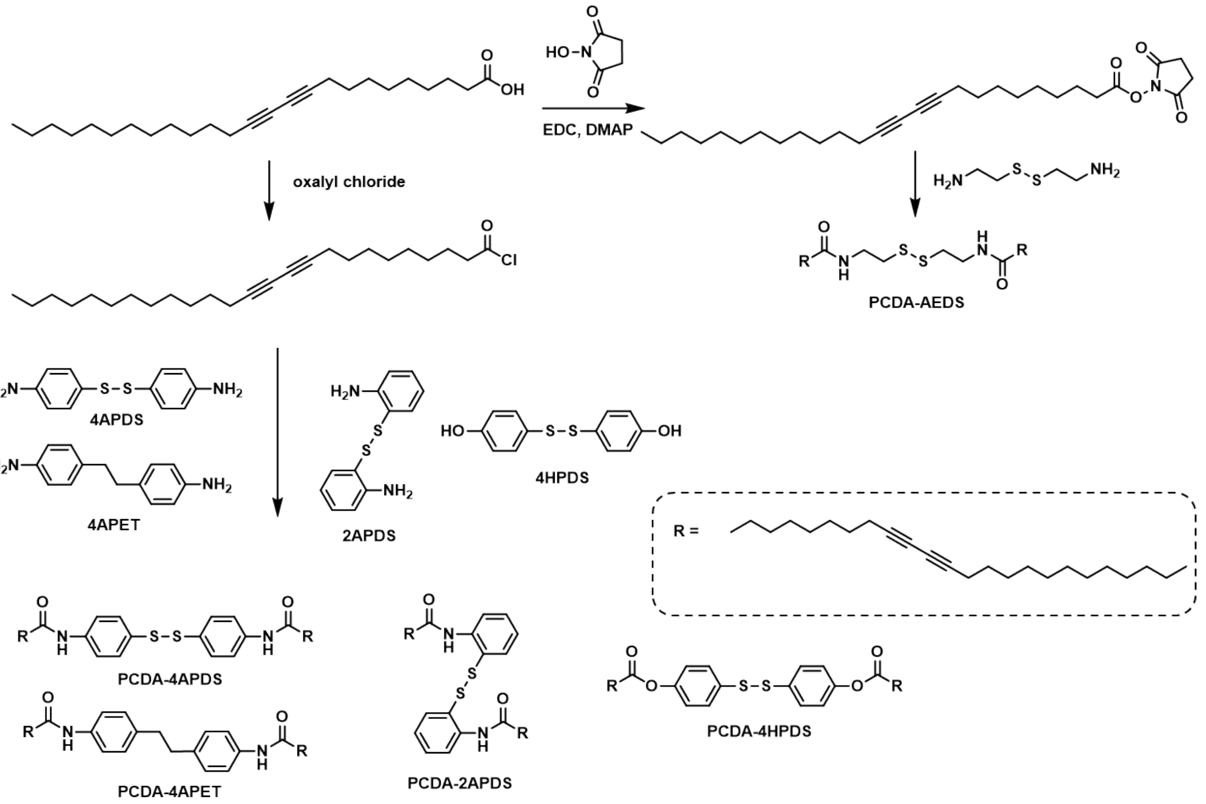
Materials. 4-Aminophenyldisulfide (4APDS), 2-aminophenyldisulfide (2-APDS), 4-hydroxyphenyldisulfide (4HPDS), 4,4'ethylenedianiline (4APET), and cystamine dihydrochloride were purchased from Aldirch-Korea. 10,12-pentacosadiynoic acid (PCDA) was obtained from GFS Chemicals. 2,5-Dioxopyrrolidin-1-yl pentacosa-10,12-diynoate (PCDA-NHS) was prepared according to the literature procedure.[1]

Instrumentation. SEM images were obtained using a HORIBA EX-250. Raman spectra were recorded on a FT-Raman spectrometer (Bruker FRA 160/S). UV-vis absorption spectra were recorded on an USB2000 miniature fiber-optic spectrometer (Ocean optics). IR spectra were recorded on a Thermo Nicolet NEXUS 470 FTIR uisng an ATR accessory (Thermo Fisher Scientific, Inc.). ^{1} H and ^{13}C NMR spectra were recorded on a Varian Unitylnova (300 MHz) spectrometer at 298 K in $CDCl_3$. Mass spectra (MS) were recorded on a SYNAPT G2 (water, U.K.) using a time-of-flight (TOF) analyzer and MALDI-TOF using AXIMA (SHIMADZU)

Synthesis of diacetylene monomers. The synthetic scheme for the preparation of diacetylene monomers investigated in this study is shown in Scheme S1. 10,12-Pentacosadiynoic acid (PCDA) was converted to the acid chloride form PCDA-Cl by treatment with oxalyl chloride. Coupling of the activated PCDA-Cl with 4-aminophenyldisulfide (4APDS), 2-aminophenyldisulfide (2-APDS), 4-hydroxyphenyldisulfide (4HPDS), and 4,4'ethylenedianiline (4APET) afforded corresponding diacetylenic monomer PCDA-4APDS, PCDA-4APET, PCDA-2APDS and PCDA-4HPDS, respectively. Direct coupling of PCDA-Cl with cystamine failed to generate the desired PCDA-AEDS due to the cleavage of the disulfide bond. Conversion of the PCDA to the neutral form of PCDA-NHS followed by reaction with cystamine yielded the desired monomer PCDA-AEDS in good yield.



Scheme S1. Synthesis of diacetylene monomers.

Synthesis of N,N'-(disulfanediylbis(4,1-phenylene))bis(pentacosa-10,12-diynamide) (PCDA-4APDS). To a solution of 10,12-pentacosadiynoic acid (PCDA) (1.0 g, 2.7 mmol) in dichloromethane (20 mL) under Ar atmosphere were added oxalyl chloride (0.44 g. 3.5 mmol) and a pipette drop of *N,N'*-dimethylformamide. The mixture was stirred overnight at room temperature and concentrated *in vacuo*. Dichloromethane (10 mL) was added to the residue and to the solution was added dropwise a dichloromethane (10 mL) solution containing triethylamine (0.4 g, 4.0 mmol) and 4-aminophenyldisulfide (0.3 g, 1.2 mmol) at 0 °C. The reaction mixture was stirred overnight at room temperature. After concentration *in vacuo*, the residue was subjected to a silica gel column chromatography (dichloromethane/methanol, 90/10 vol%) to yield the desired product **PCDA-4APDS** (1.15 g, 90%).

m.p (143 °C); ^{1}H NMR (600 MHz, THF): 9.03 (s, 2H), 7.59 (d, *J* = 2.4 Hz, 4H), 7.37 (d, *J* = 4.8, 4H), 2.28 (t, *J* = 6.0 Hz, 4H), 2.24 (t, *J* = 4.8, 8H), 1.57-1.25 (m, 64H), 0.88 (t, *J* = 6.6, 6H); ^{13}C NMR (75 MHz, THF): δ 171.6, 141.7, 131.8, 120.1, 77.8, 66.4, 37.9, 33.1, 30.6, 30.5 30.4 30.3, 30.2, 30.1, 30.0, 29.8, 29.4, 26.2, 23,6 19.8, 14,4; IR (KBr) vcm^{-1}: 3294, 2920, 2848, 1659, 1585, 1526, 1491, 1461, 1392, 1301, 1250, 1178, 817, 724, 505,; MS (MALDI-

TOF): calcd. for $C_{62}H_{92}N_2O_2S_2Na^+$ $[M+Na]^+$ 982.64, found 983.15. By employing the similar protocol **PCDA-APET**, **PCDA-2APDS**, and **PCDA-4HPDS** were prepared.

N,N'-(Ethane-1,2-diylbis(4,1-phenylene))bis(pentacosa-10,12-diynamide) (PCDA-4APET) (yield: 85%). m.p (146 °C); ^{1}H NMR (300 MHz, THF): 8.77 (s, 2H), 7.49 (d, *J* = 8.7 Hz, 4H), 7.35 (d, *J* = 8.7, 4H), 2.80 (s, 4H), 2.27-2.20 (m, 12H), 1.69-1.29 (m, 64H), 0.88 (t, *J* = 6.9, 6H); ^{13}C NMR (75 MHz, THF): δ 170.5, 157.7, 138.3, 136.6, 128.8, 119.2, 77.0, 37.95, 37.231, 32.41, 30.129, 30.00, 29.84, 29.81, 29.61, 29.50, 29.30, 28.95, 25.9, 23.10, 19.12, 13.97, 13.63; IR (KBr) νcm^{-1}: 3280, 2919, 2847, 1655, 1610, 1595, 1534, 1465, 1407, 1320, 1304, 1255, 1180, 830, 721; MS (MALDI-TOF): calcd. for $C_{64}H_{95}N_2O_2Na^+$ $[M+Na]^+$ 946.73, found 946.87.

N,N'-(Disulfanediylbis(2,1-phenylene))bis(pentacosa-10,12-diynamide) (PCDA-2APDS) (yield: 65%). m.p (87 °C); ^{1}H NMR (300 MHz, $CDCl_3$): 8.40 (d, *J* = 6.0 Hz, 2H), 7.96 (s, 2H), 7.40 (t, *J* = 7.8, 4H), 7.02 (t, *J* = 6.6 Hz, 2H), 2.23 (m, 8H), 2.15 (t, *J* = 6.9 Hz, 4H), 1.61 (m, 64H), 0.88 (t, *J* = 6.3, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.9, 140.5, 137.1, 132.8, 124.7, 124.0, 121.5, 65.9, 65.8, 38.3, 32.5, 30.2, 30.1, 29.9, 29.8, 29.7, 29.5, 29.4 29.3, 28.9, 25.9, 23.3, 19.8, 14.7; IR (KBr) νcm^{-1}: 3274, 2920, 2848, 1666, 1578, 1532, 1465, 1439, 1421, 1290, 1248, 1176, 739.89; MS (MALDI-TOF): calcd. for $C_{62}H_{92}N_2O_2S_2Na^+$ $[M+Na]^+$ 982.64, found 982.86.

Disulfanediylbis(4,1-phenylene) bis(pentacosa-10,12-diynoate) (PCDA-4HPDS) (yield: 72%). m.p (69 °C); ^{1}H NMR (300 MHz, $CDCl_3$): 7.48 (d, *J* = 5.7 Hz, 4H), 7.03 (d, *J* = 8.7 Hz, 4H), 2.53 (t, *J* = 7.5, 4H), 2.24 (t, *J* = 6.3 Hz, 8H), 1.73-1.26 (m, 64H), 0.88 (t, *J* = 6.6, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 150.5, 134.1, 129.6, 122.5, 65.5, 65.4, 34.5, 32.1, 29.8, 29.6, 29.5, 29.3, 29.2, 29.0, 28.9, 28.5, 28.4, 25.0, 22.8, 19.4, 18.5, 14.3; IR (KBr) νcm^{-1}: 2917, 2849, 1747, 1487, 1469, 1418, 1379, 1326, 1248, 1208, 1166, 1144, 1096, 842, 829, 717; MS (MALDI-TOF): calcd. for $C_{62}H_{89}O_4S_2Na^+$ $[M+Na]^+$ 984.61, found 983.53.

Synthesis of N,N'-(disulfanediylbis(ethane-2,1-diyl))bis(pentacosa-10,12-diynamide) (PCDA-4AEDS). To a solution of 2,5-dioxopyrrolidin-1-yl pentacosa-10,12-diynoate (PCDA-NHS) (1.0 g, 2.1 mmol) in dichloromethane (20 mL) under Ar atmosphere were added dropwise a dichloromethane (10 mL) solution containing triethylamine (0.3 g, 2.5 mmol) and cystamine hydrochloride (0.2 g, 1.0 mmol) at 0 °C. The reaction mixture was stirred overnight at room temperature. After concentration *in vacuo*, the residue was subjected to a silica gel column chromatography (dichloromethane/methanol, 90/10 vol%) to yield the desired product **PCDA-4AEDS** (0.64 g, 72 %).

m.p (113 ^{o}C) ^{1}H NMR (300 MHz, $CDCl_3$): 6.25 (s, 2H), 3.57 (q, J = 6.0 Hz, 4H), 2.82 (t, J = 4.8, 4H), 2.20 (m, 12H), 1.65-1.26 (m, 64H), 0.88 (t, J = 6.0, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.4, 109.7, 65.0, 64.9, 38.1, 37.6, 36.3, 31.6, 29.4, 29.2, 29.1, 28.9, 28.8, 28.7, 28.6, 28.5, 28.1, 28.0, 25.4, 22.4, 18.9, 13.9; IR (ATR) vcm^{-1}: 3350, 3295, 2918, 2849, 1637, 1543, 1469, 1420, 1256, 1219, 1193, 720; MS (MALDI-TOF): calcd. for $C_{54}H_{91}N_2O_2S_2Na^+$ $[M+Na]^+$ 886.64, found 886.45

Polymerization of each monomer. PCDA-4APDS and **PCDA-4APET** were polymerized by heating the monomer powder in a glass petri dish sealed with aluminum foil on a hot plate at 140 ^{o}C for 12 h. Polymers of **PCDA-2APDS** and **PCDA-4AEDS** were obtained by 254 nm UV irradiation (1 mW/cm^2) of the monomer powder. In order to increase the degree of polymerization, repeated UV irraiation was conducted with stirring and mixing of the monomer. Polymers obtained with **PCDA-4APDS**, **PCDA-4APET**, **PCDA-2APDS** and **PCDA-4AEDS** displayed an intense blue color suitable for the mechanochromic test. The diacetylene monomer **PCDA-4HDPS** showed no sign of polymerization eithe by themal treatment or by UV irradiation.

Mechanochromic test. Polymerized **PCDA-4APDS** powder was placed in a ceramic crucible and mechanically ground with hand. Temperature of the sample during the grinding process was monitored with an infrared thermometer and a metal resistant thermometer to keep the sample temperature below the thermochromic temperature of the polymer. Annealing of the polymer was carried out by placing the mechanically ground sample in a glass petri dish sealed with aluminum foil on a hot plate at 140 ^{o}C for 6 h. The red-colored sample turned blue immediately upon cooling back to 25 ^{o}C.

References

(1) J.-M. Kim; E.-K. Ji; S.M. Woo; H. Lee; D.J. Ahn, *Adv. Mater.* 2003, **15**, 1118

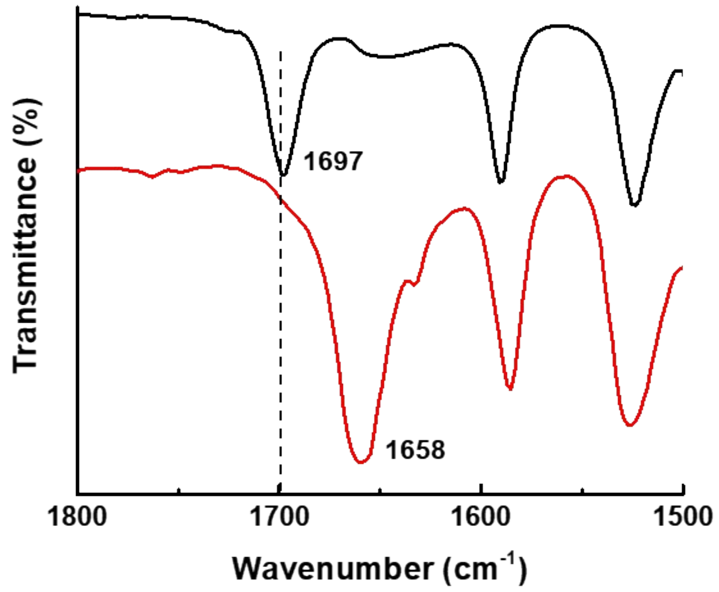


Figure S1. FTIR spectra of PCDA-4APDS in the carbonyl absorption region in the solution (black line, tetrahydrofuran) and solid (red line) state.

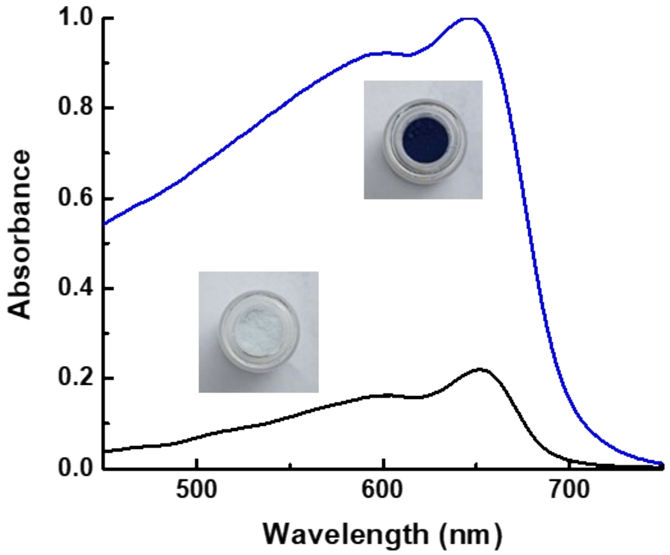


Figure S2. UV-vis absorption spectra of PCDA-4APDS before (black line) and after (blue line) polymerization (140 ^{o}C, 24 h). Images in the insets show the color change taking place in the PCDA-4APDS powder.

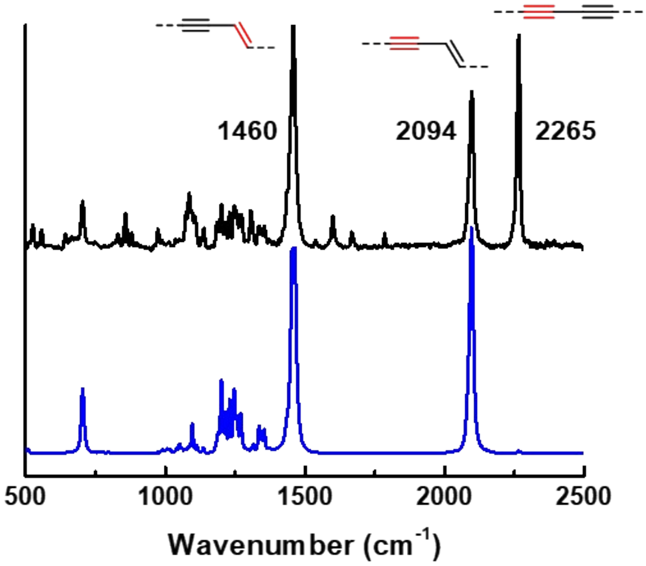


Figure S3. Raman spectra of PCDA-4APDS powder before (black line) and after heating (blue line) at 140 °C for 24 h.

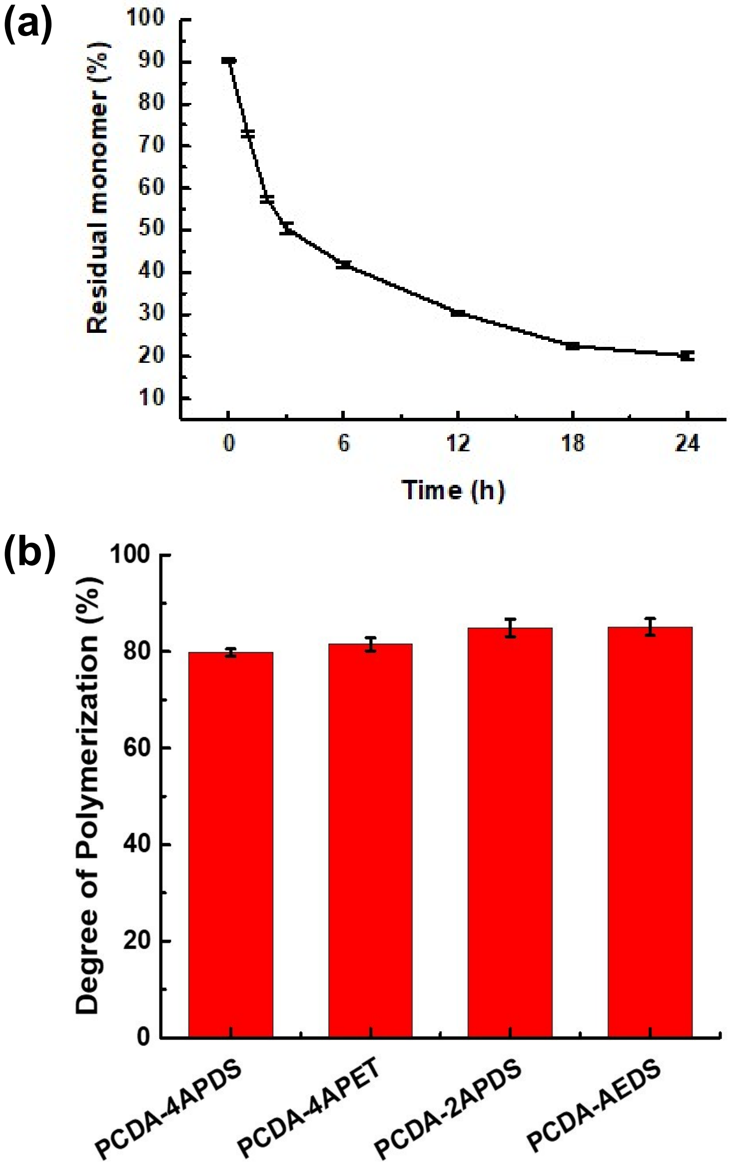


Figure S4. (a) Residual monomer (%) as a function of heating time for PCDA-4APDS. (b) Degree of Polymerization (%) for PCDA-4APDS, PCDA-4APET, PCDA-2APDS and PCDA-AEDS.

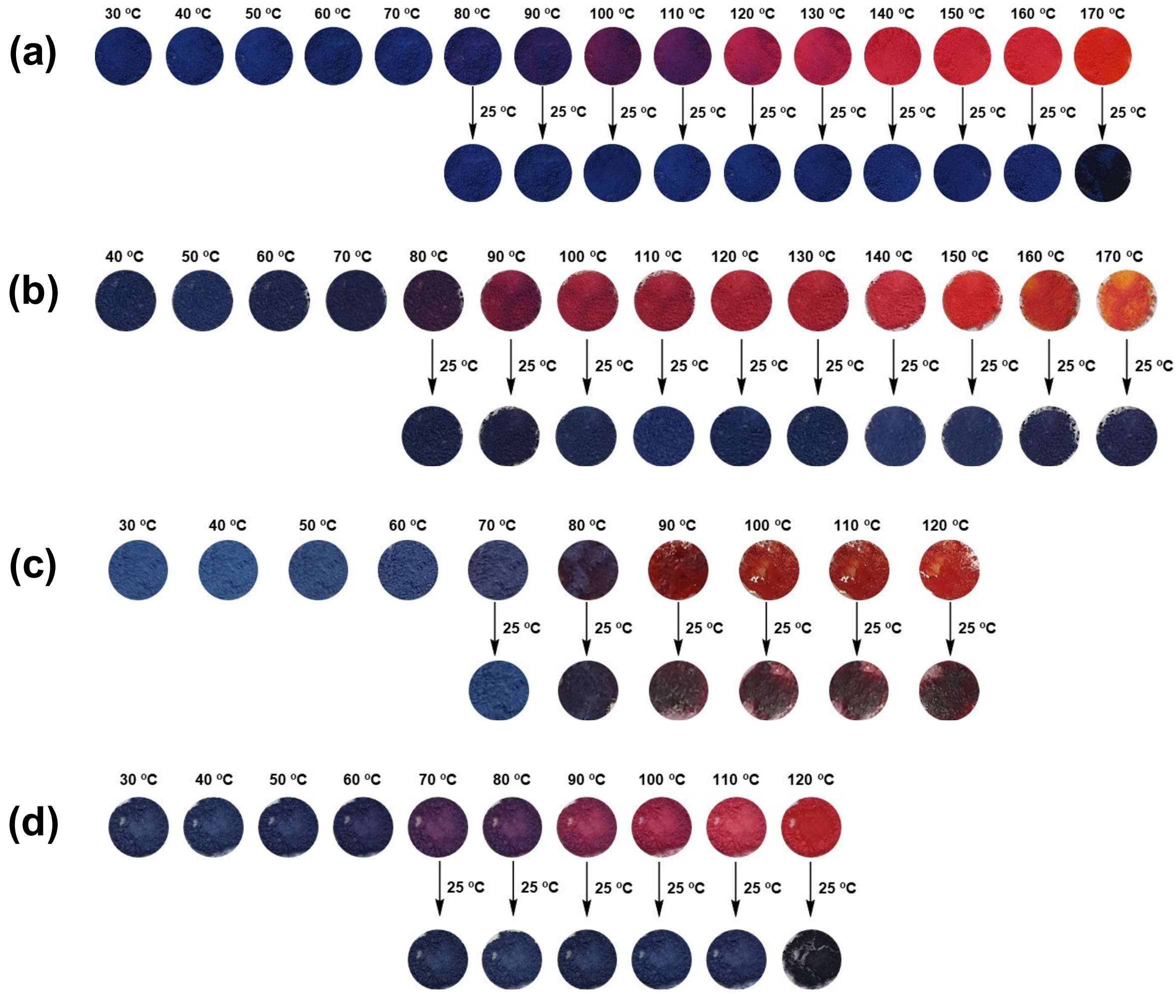


Figure S5. Photographs of polymerized PCDA-4APDS (a), PCDA-4APET (b), PCDA-2APDS (c) and PCDA-4AEDS (d) upon heating and cooling.

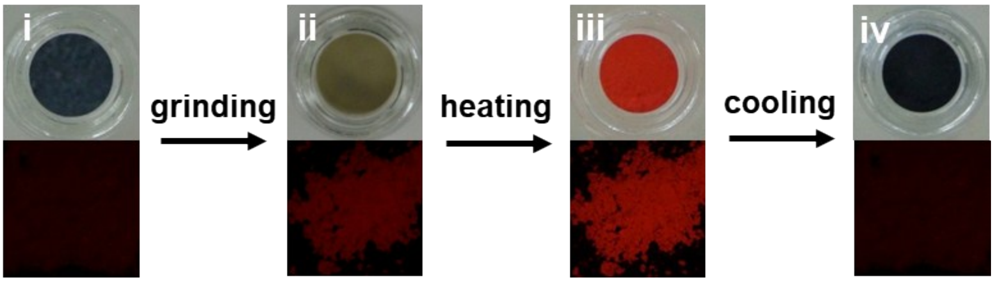


Figure S6. Photographs (above) and fluorescence (bottom) images of a polymerized PCDA-4APDS powder as prepared (i), after grinding (ii) after thermal treatment of the ground sample at 140 °C for 6 h (iii) and subsequent cooling to 25 °C (iv).

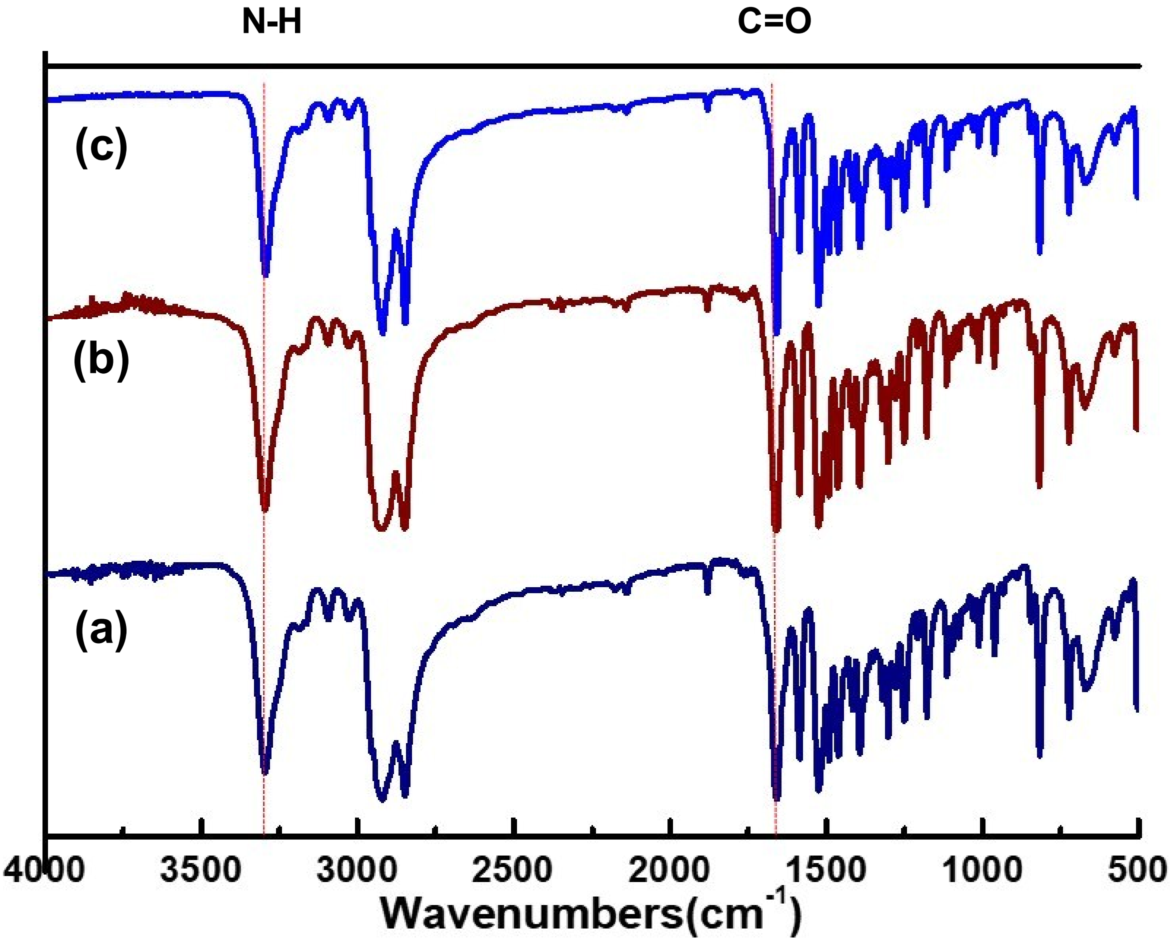


Figure S7. FTIR spectra of the PCDA-4APDS-derived polymer as prepared (a), after grinding (b) and after annealing at 140 °C for 6 h (c).

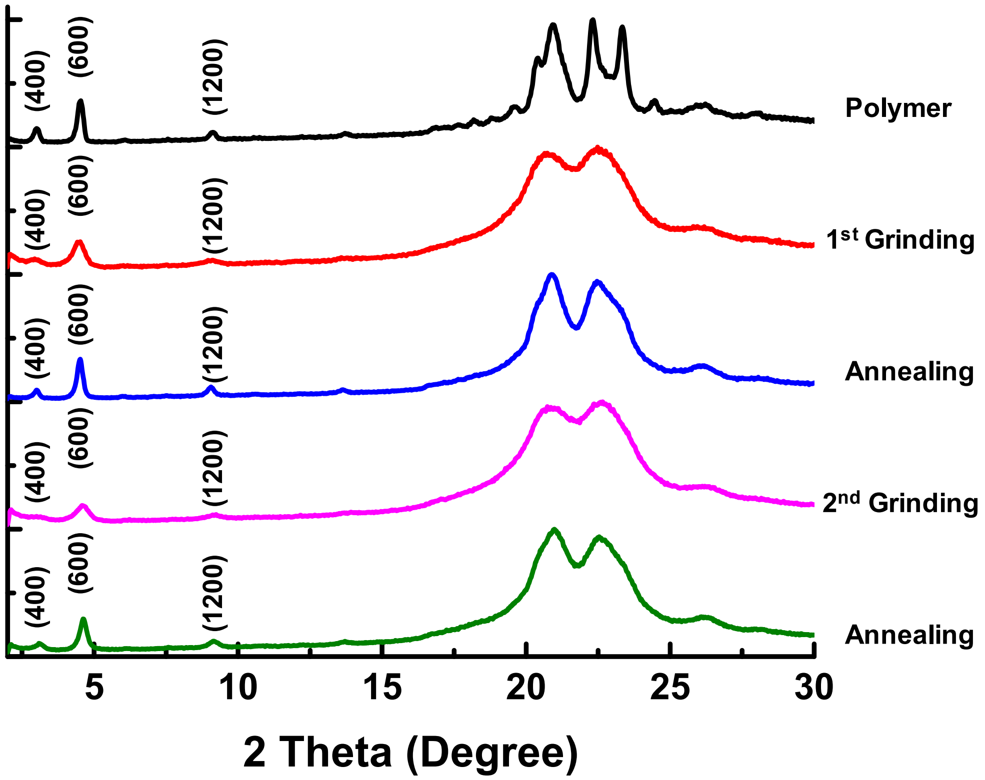


Figure S8. Powder X-ray diffraction spectra of the PCDA-4APDS-derived polymer as prepared (a), after grinding (b) and after annealing at 140 °C for 6 h (c).

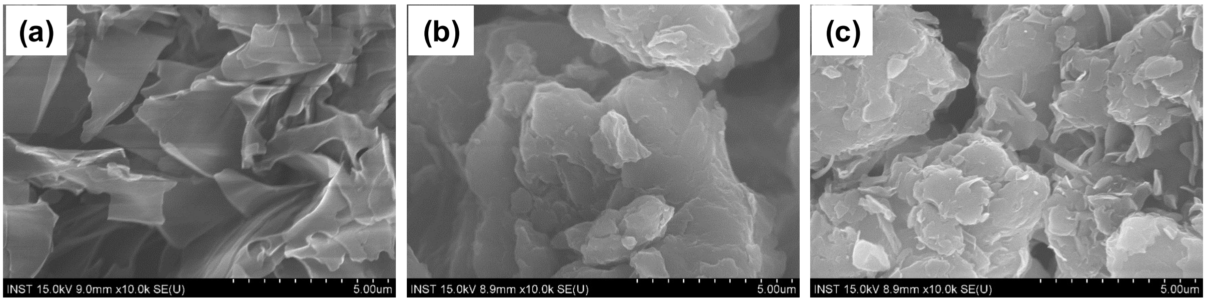


Figure S9. SEM images of the PCDA-4APDS-derived polymer as prepared (a), after grinding (b) and after annealing at 140 ^{o}C for 6 h (c).

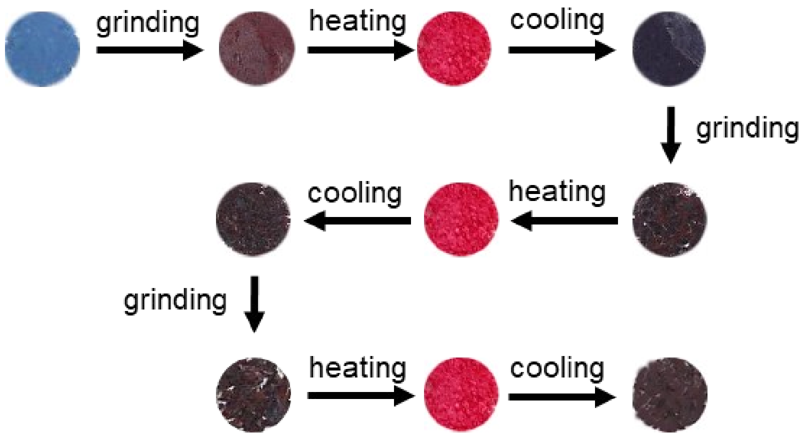


Figure S10. Photographs of the polymerized PCDA-4APET during the mechanochromic-annealing cycles.

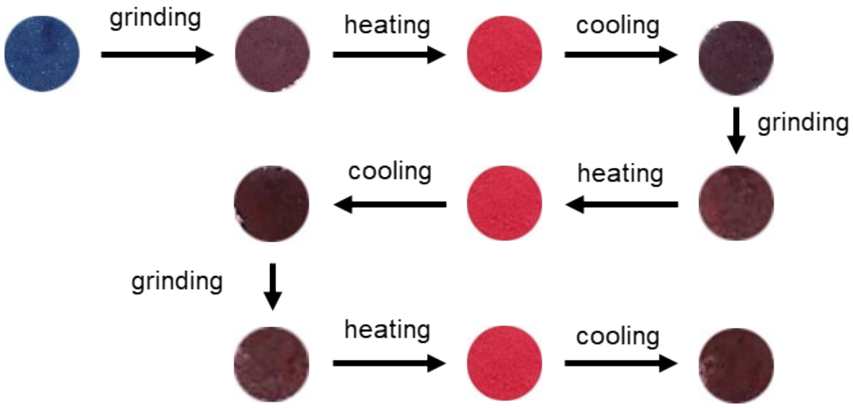
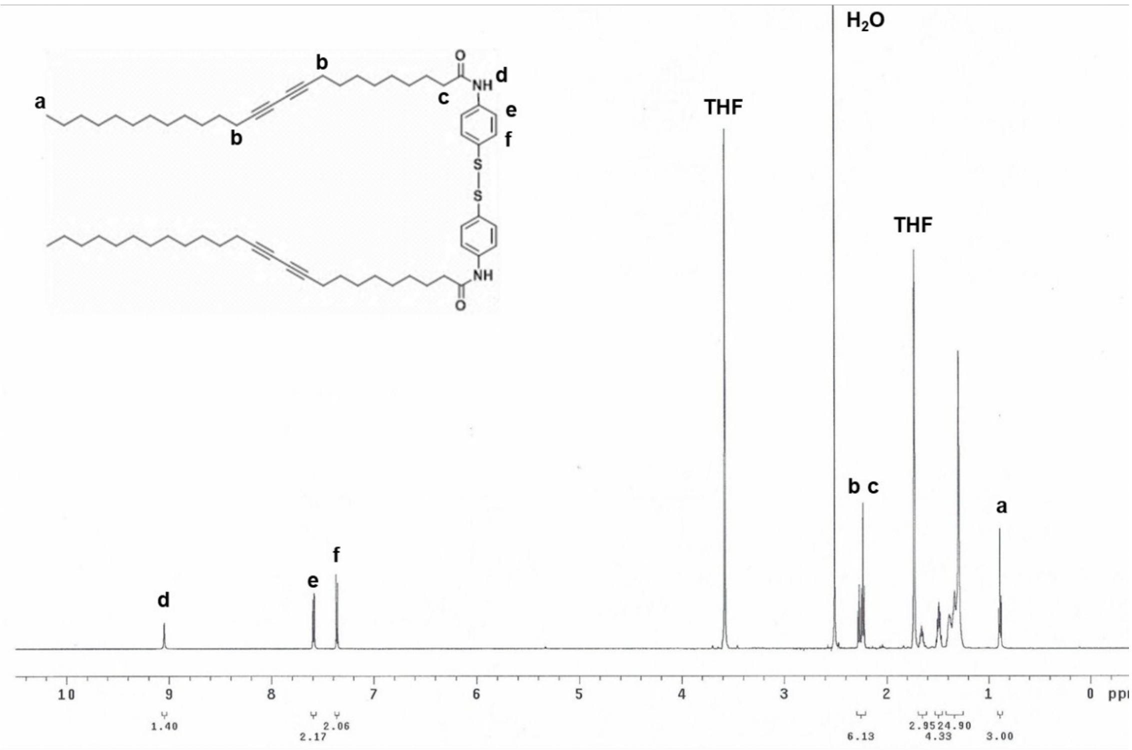


Figure S11. Photographs of the polymerized PCDA-AEDS during the mechanochromic-annealing cycles.



^{13}C NMR

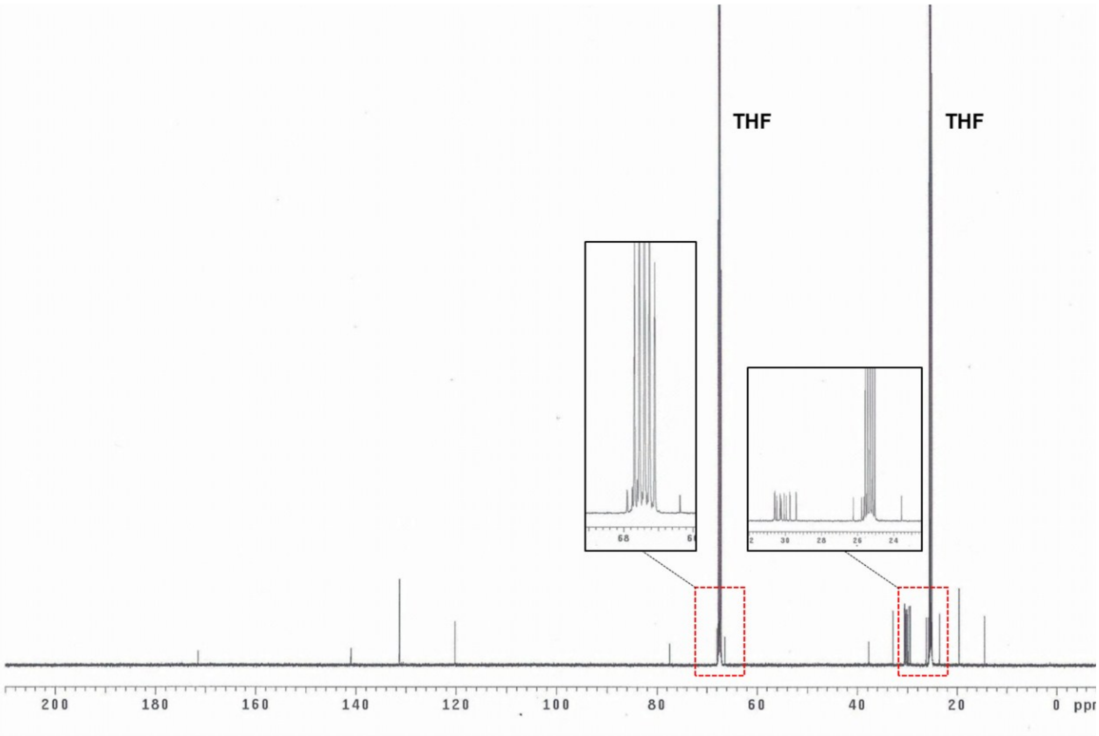


Figure S12. ^{1}H (top, 600 MHz) and ^{13}C (bottom, 150 MHz) NMR spectra of **PCDA-4APDS** in THF-d_8..

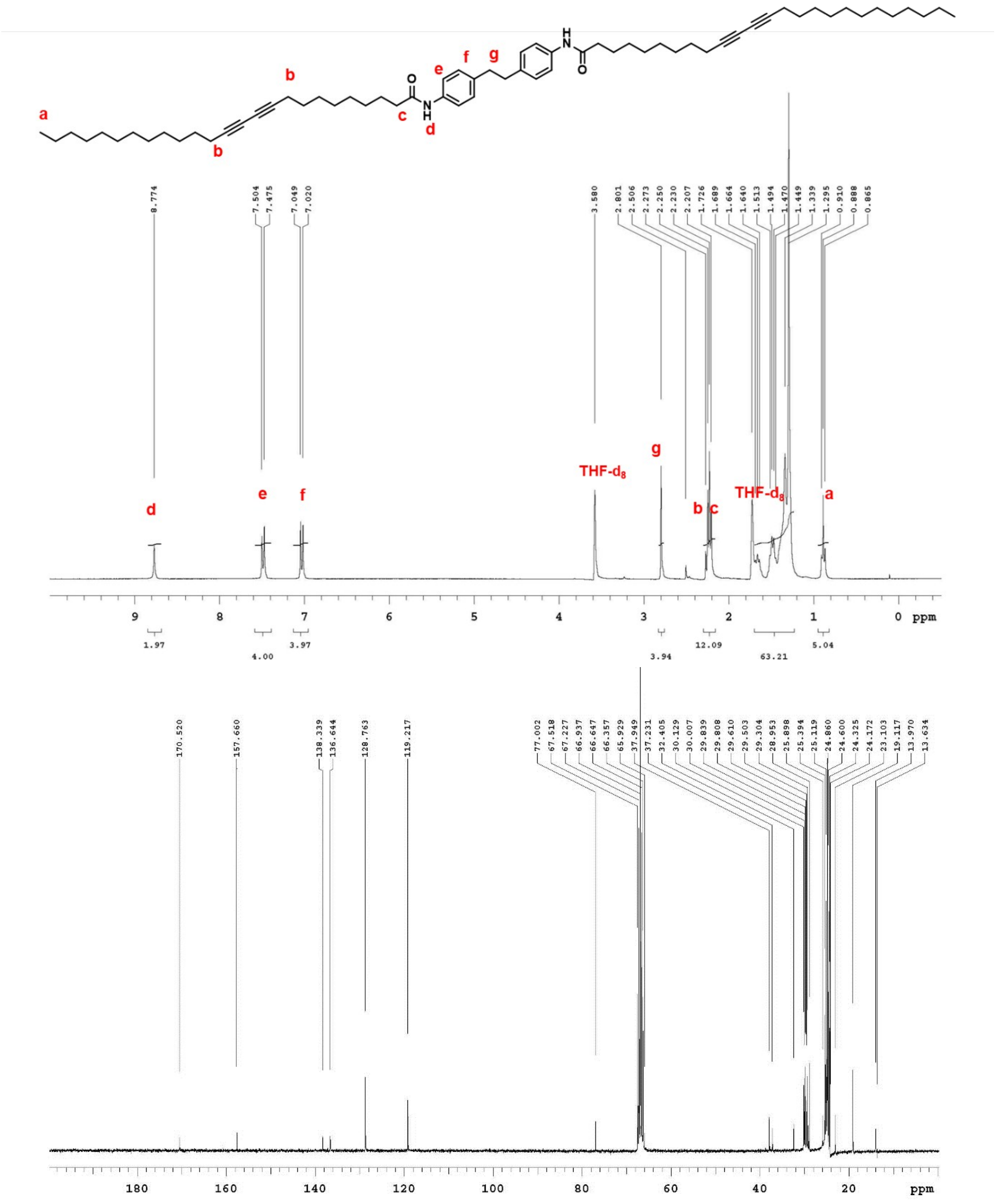


Figure S13. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **PCDA-4APET** in THF-d_8

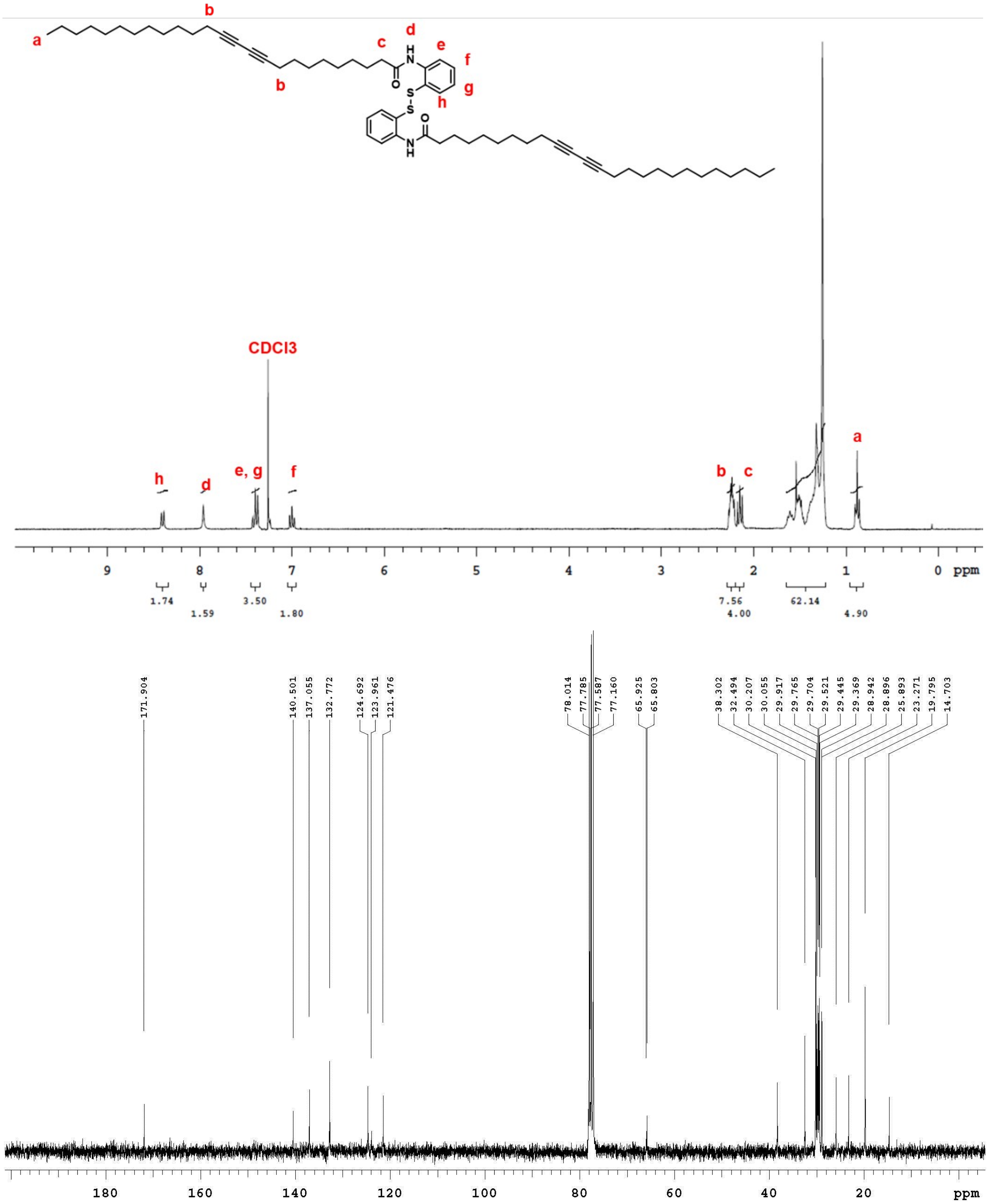


Figure S14. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **PCDA-2APDS** in $CDCl_3$.

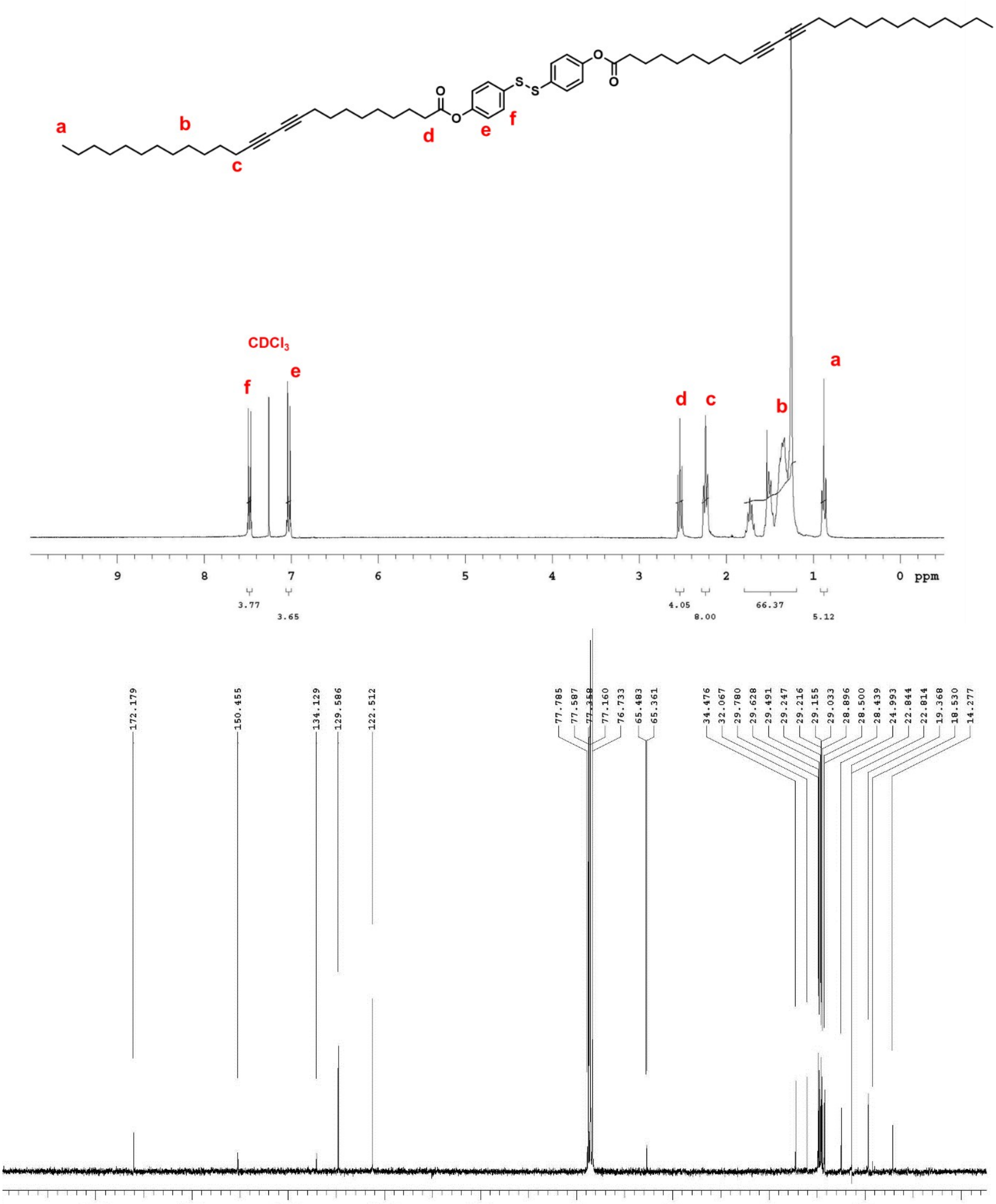


Figure S15. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **PCDA-4HPDS** in CDCl$_3$.

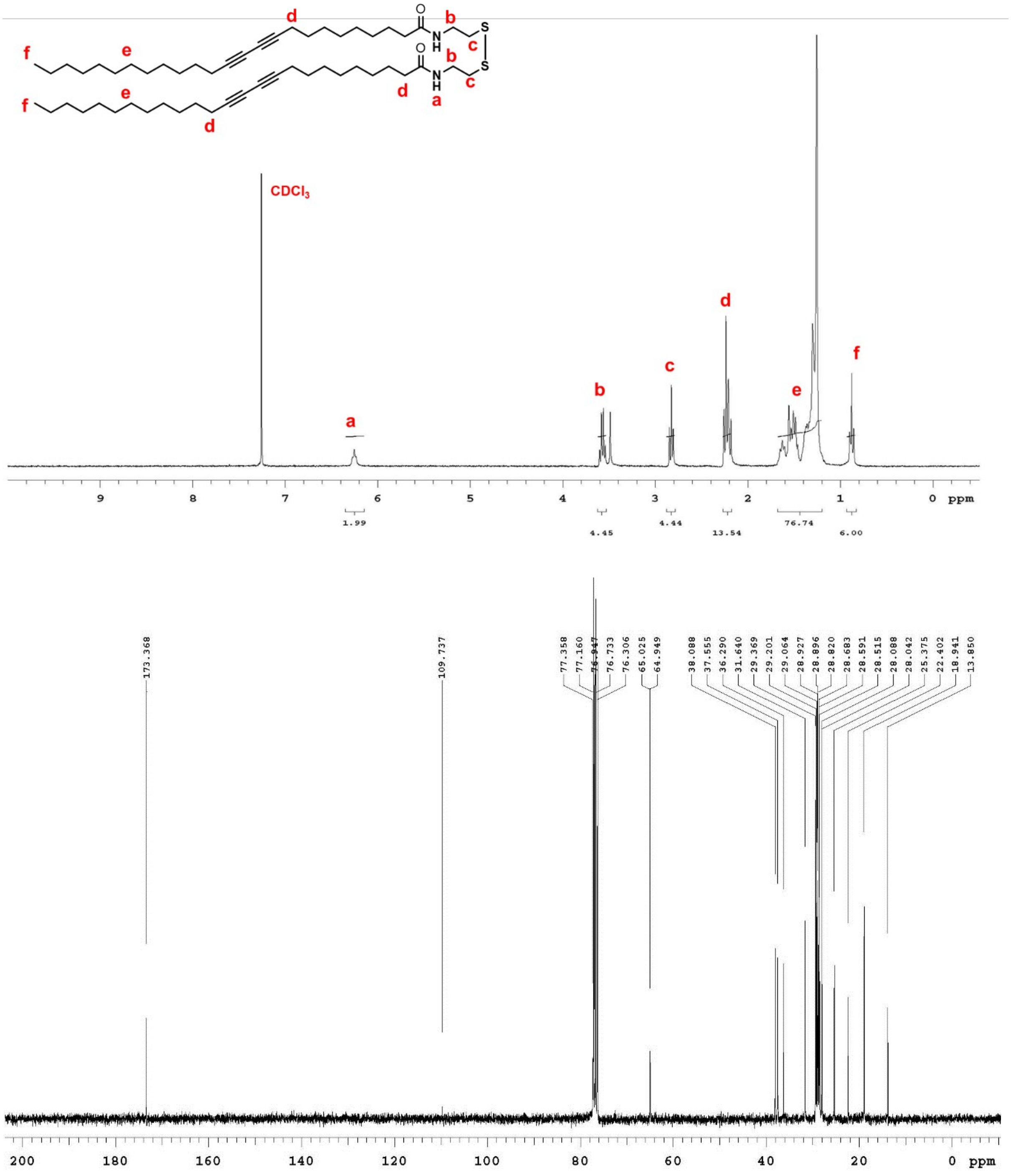


Figure S16. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **PCDA-4AEDS** in $CDCl_3$.