Electronic supplementary information (ESI)

A facile synthesis of a novel triptycene-containing A-B monomer: precursor to polymers of intrinsic microporosity

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1. Materials and Methods:

Melting points were determined on an Electrothermal Eng. Ltd melting point apparatus and are uncorrected. All NMR spectra were recorded on a Bruker DRX 400 spectrometer (400 MHz) in the suitable solvent using TMS as the internal standard. Chemical shifts (δ) are reported in ppm. Infra-red spectra were performed using Shimadzu FT-IR-8400S Fourier transform infrared spectrophotometer. Elemental analyses were obtained using a Carlo Erba Instrument CHNS-O EA108 elemental analyzer. Low temperature (77 K) N_2 adsorption/desorption study of the polymer powder was undertaken using Beckman Coulter 3100 Surface Area Analyzer (Fullerton, California, USA). Apparent surface area of the polymer was calculated from N_2 adsorption data by multipoint BET analysis. GPC analyses were carried out on Viscotek GPCmax VE2001 with RI(VE3580) detector, using chloroform as eluent; Columns: KF-805L SHODEX, Temperature: ambient; Flow rate of 1 ml/min; Calibration: a series of polystyrene standard up to Mw: 9.4 x10^5 with a narrow polydispersity. Thermogravimetric analysis (TGA) measurements were obtained using TA Instruments SDT Q600 Analyzer fitted with double beam microbalance (0.1µg sensitivity). All analyses were performed at heating rate of 10 °C/min from 40 to 1000 °C. Experimental details, procedures and full characterizations of the new synthesized compounds and the polymer obtained from A-B monomer **8** are described below.

2. Monomer synthesis

2.1 Synthesis of 2,3,6,7-Tetramethoxy-9,10-dibutylanthracene 4.

2,3,6,7-Tetramethoxy-9,10-dibutylanthracene **4** was prepared according to the procedure described by Ghanem et al [1], as follows: A cooled mixture of veratrole (0.1 mol), valeraldehyde (0.1 mol) and CH_3CN (0.1 mol) was added dropwise at 0-5 ^oC to a stirred and cooled concentrated H_2SO_4 (50 ml) over a period of 30 minutes. The reaction mixture was then stirred at room temperature for two hours and poured into ice-cold water. The precipitate formed was filtered and washed with copious amounts of water and recrystallized from acetone to give yellow crystals.

2.2 Synthesis of 2,3,6,7-Tetramethoxy-9,10-dibutyltriptycene 5.

2,3,6,7-tetramethoxy-9,10-dibutyltriptycene was prepared according to the procedure of Zong et al[2], as follows: A mixture of 2,3,6,7-tetramethoxy-9,10-dibutylanthracene (1.6 gm, 4.9 mmol) and the premade 2-carboxy-benzenediazonium chloride (3.5 gm, 19 mmole) in dichloroethane (60 ml) and 1,2-epoxypropane (5 ml) was refluxed for 4 hrs under nitrogen atmosphere. On cooling, the reaction mixture was filtered and concentrated under reduced pressure. The crude product was washed with methanol and collected by filtration, purified by column chromatography over silica gel (eluent: DCM). Recrystallization from ethanol-water give colourless crystals, M.P = 144-146 ^{o}C. Elemental Analysis; (Found C, 78.98; H, 7.87. Calc. for $C_{32}H_{38}O_4$: C, 79.27; H, 8.29 %). ^{1}H-NMR (400 MHz; $CDCl_3$): δ (ppm): 1.09 (t, 6H), 1.77 (m, 4H), 2.08 (m, 4H), 2.79 (t, 4H), 3.75 (s, 12H), 6.9 (m, 6H), 7.27 (m, 2H). ^{13}C-NMR (100 MHz; CDCl3) δ (ppm): 14.5, 25.2, 28.0, 28.4, 52.6, 56.3, 107.6, 121.5, 124.2, 141.6, 145.4, 149.2. Mass: *m/z*, LRMS (EI/CI): 487 (M^{+}+1), 504.34 (M^{+}+NH_4),

2.3. Synthesis of o-quinone 6.

o-quinone **6** was prepared according to the literature procedure described by Zhao et al[3], as follows: To a stirred solution of tetramethox-9,10-dibutyl triptycene (2.24 mmole) in 60 ml (1:1 v/v , DCM, HOAC) was added 1 ml of nitric acid (68 %) dropwise. The reaction mixture was then stirred at room temperature for 5 minutes and poured to 150 ml ice-cooled water. The product was extracted with DCM, washed with 10 % $NaHCO_3$ solution and dried over anhydrous magnesium sulphate. The organic layer was evaporated to dryness and purified by column chromatography (silica gel) using DCM as an eluent and recrystallized from DCM/pet.ether (40-60 ^{o}C) to afford red crystals, (83 % yield), M.P = 167- 169 °C. Elemental Analysis; (Found C, 78.71; H, 7.197. Calc. for $C_{30}H_{32}O_4$: C, 78.92; H, 7.06 %). ^{1}H-NMR (400 MHz; $CDCl_3$) δ (ppm): 1.14 (t, *J* = 7.2 Hz, 6H, CH_3), 1.79 (sixtet, *J* = 7.2 Hz, 4H, CH_2), 1.93-2.12 (m, 4H), 2.50-2.70 (m, 4H), 3.91 (s, 6H), 6.13 (s, 2H), 6.97 (s, 2H), 7.30-7.38 (m, 2H), 7.40-7.50 (m, 2H). IR (KBr, cm^{-1}): 1684 (conj. CO). ^{13}C-NMR (100

MHz; $CDCl_3$) δ (ppm): 14.3, 24.6, 27.3, 27.7, 50.9, 56.2, 107.6, 118.5, 123.5, 127.7, 132.2, 139.9, 148.9, 157.3, 180.2; Mass: *m/z*, LRMS (AP+): 457 (M^++1).

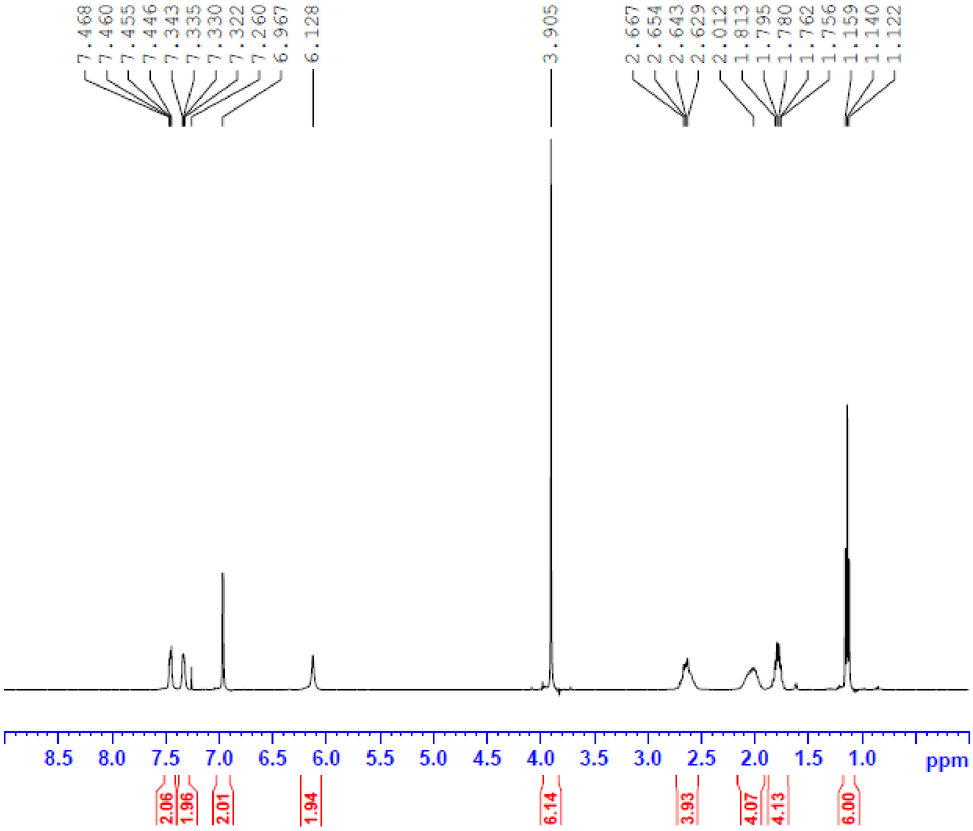

Figure S1. ^{1}H-NMR spectrum ($CDCl_3$) for 9, 10-dibutyl-o-quinone **(6)**

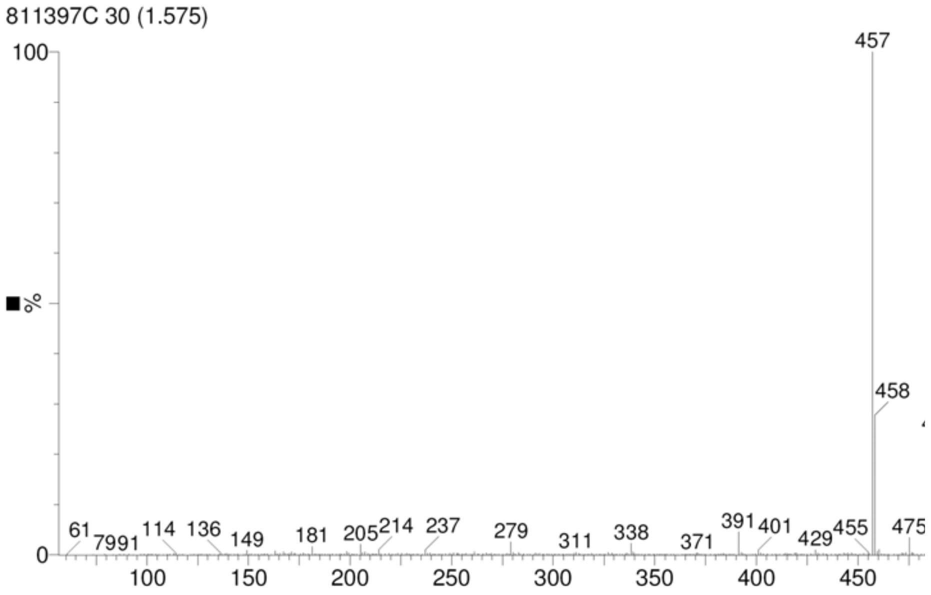

Figure S2. LRMS (AP+) for 9, 10-dibutyl-o-quinone **(6)**

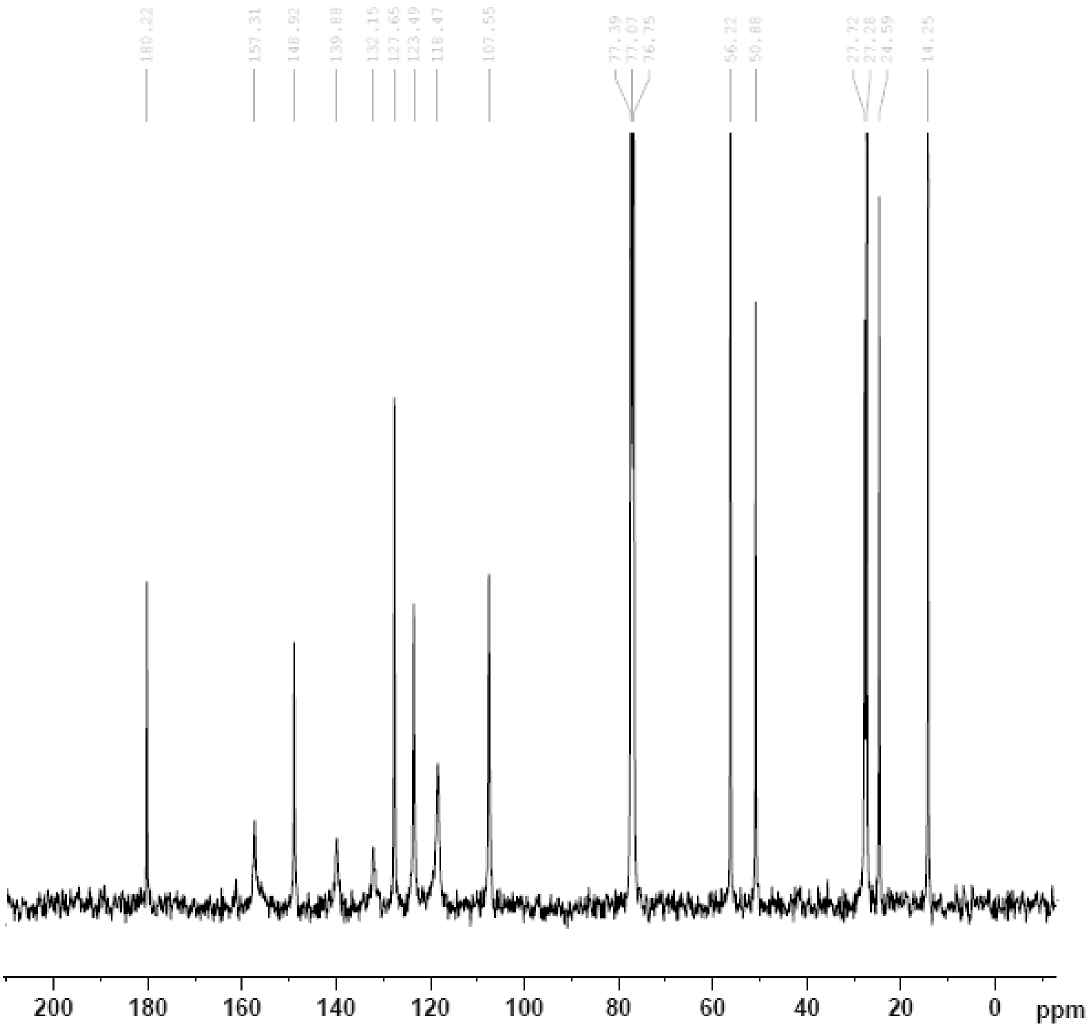

Figure S3. ^{13}C-NMR spectrum ($CDCl_3$) for 9, 10-dibutyl-o-quinone **(6)**

2.4. Synthesis of o-dichloro compound 7.

A mixture of 9,10-dibutyl-o-quinone (3.22 mmol) and 4,5-dichlorobenzene-1,2-diamine (3.38 mmol) in glacial acetic acid (50 ml) was heated under reflux for 2 hours under nitrogen atmosphere. On cooling, the reaction mixture was concentrated under reduced pressure and the crude product was collected and purified by column chromatography (silica gel) using DCM as an eluent to afford yellow crystals (89 % yield), M.P = 192-195 ^{o}C. Elemental Analysis; (Found C, 71.73; H, 5.69; N, 4.67. Calc. for $C_{36}H_{34}Cl_2N_2O_2$: C, 72.36; H, 5.73; N, 4.69 %). ^{1}H-NMR (400 MHz; $CDCl_3$) δ (ppm): 1.23 (t, *J* = 7.2 Hz, 6H), 1.91 (sixt, *J* = 7.2 Hz 4H), 2.15-2.35 (m, 4H), 2.96-3.11 (m, 4H), 3.87 (s, 6H), 7.09 (s, 2H), 7.10-7.20 (m, 2H), 7.45-7.55 (m, 2H), 7.8-8.0 (m, 2H), 8.23 (s, 2H). ^{13}C-NMR (100 MHz; $CDCl_3$) δ (ppm): 14.3, 25.3, 27.5, 28.4, 52.3, 56.2, 108.0, 120.1, 122.9, 125.7, 129.5, 134.3, 137.8, 141.6, 143.0, 145.3, 146.8, 152.3 .

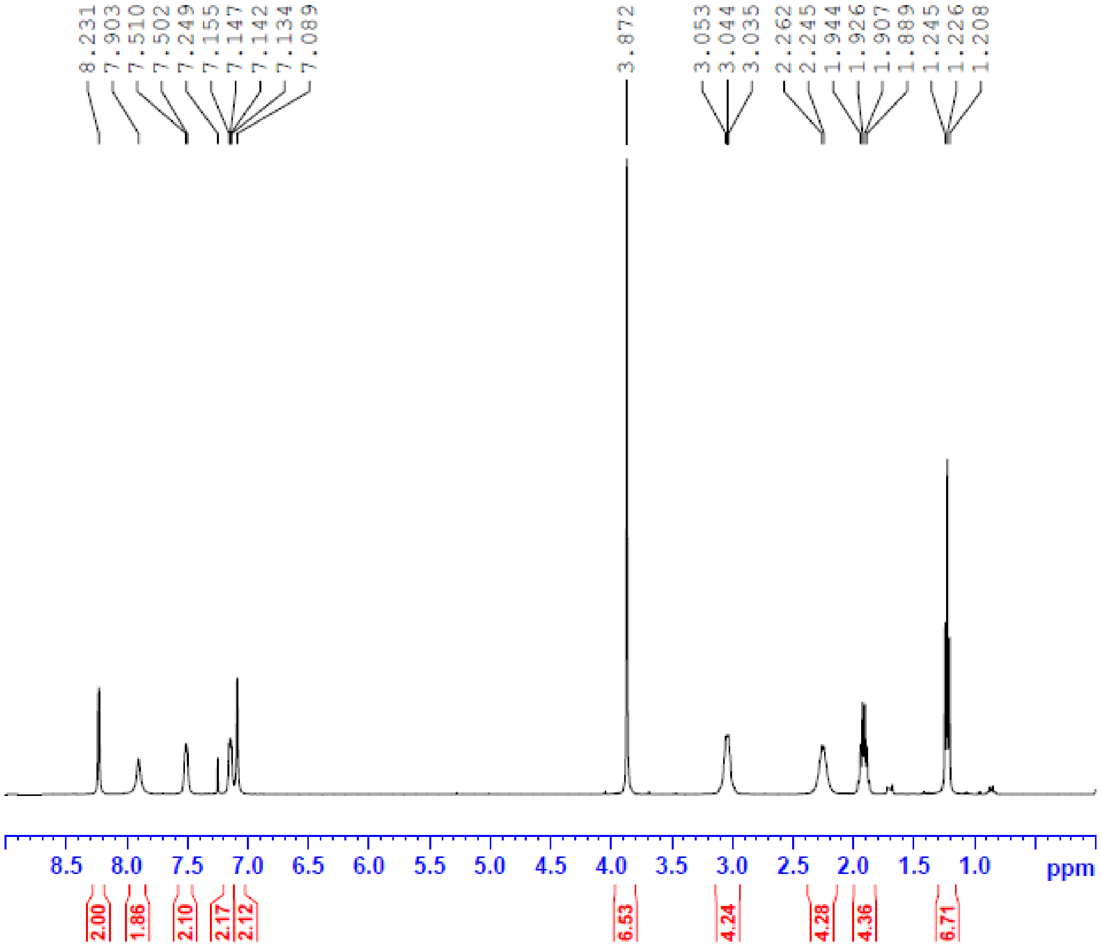

Figure S4. ^{1}H-NMR spectrum ($CDCl_3$) for compound **(7)**

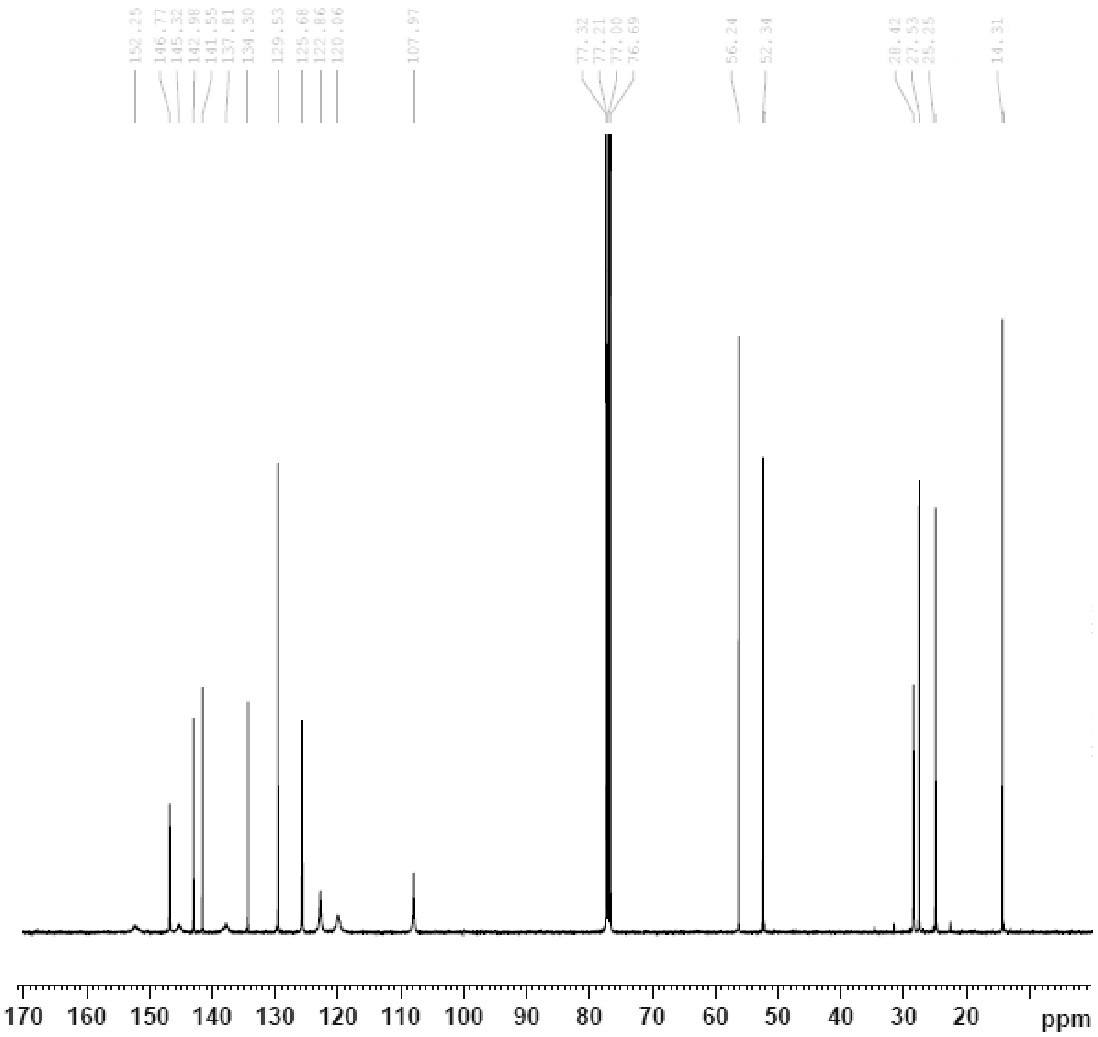

Figure S5. ^{13}C-NMR spectrum ($CDCl_3$) for compound **(7)**

2.5. Synthesis of the A-B monomer 8.

Boron tribromide (4 mmole) was added dropwise to an ice-cooled solution of compound **7** (2.32 mmole) in dry dichloromethane (40 ml) and under nitrogen atmosphere. After addition, the reaction mixture was warmed to room temperature and kept at this temperature for 2 hours. The deep orange solution was poured onto cooled water and the DCM was evaporated under vacuum. The resulting precipitate was removed by filtration, washed with cold water and dried. The crude product was finally recrystallized from THF/petroleum ether (40-60 °C) to give an orange-red powder (85 % yield), M.P = 306 - 308 °C. Elemental Analysis; (Found C, 71.57; H, 5.79; N, 4.78. Calc. for $C_{34}H_{30}Cl_2N_2O_2$.0.5 THF: C, 71.4; H, 5.66; N, 4.62 %).

^{1}H-NMR (400 MHz; DMSO-d6) δ (ppm): 1.18 (t, *J* = 7.6 Hz, 6H), 1.86 (sixt, *J* = 7.6 Hz, 4H), 2.08 (pent, *J* = 6.8 Hz 4H), 2.82-3.00 (m, 4H), 6.97 (s, 2H), 7.14-7.20 (m, 2H), 7.41-7.52 (m, 2H), 7.68-7.82 (m, 2H), 8.28 (s, 2H), 8.92 (br s, 2H); ^{13}C-NMR (100 MHz; DMSO-d6) δ (ppm): 14.3, 24.2, 25.1, 27.0, 27.8, 51.4, 111.5, 118.8, 122.7, 125.4, 129.3, 132.7, 135.7, 140.9, 142.1, 142.6, 145.1, 152.3; IR (KBr, cm^{-1}): 3074 (arom.CH), 3466 (OH); Mass: *m/z*, LRMS (AP$^+$): 570 (M$^+$+1).

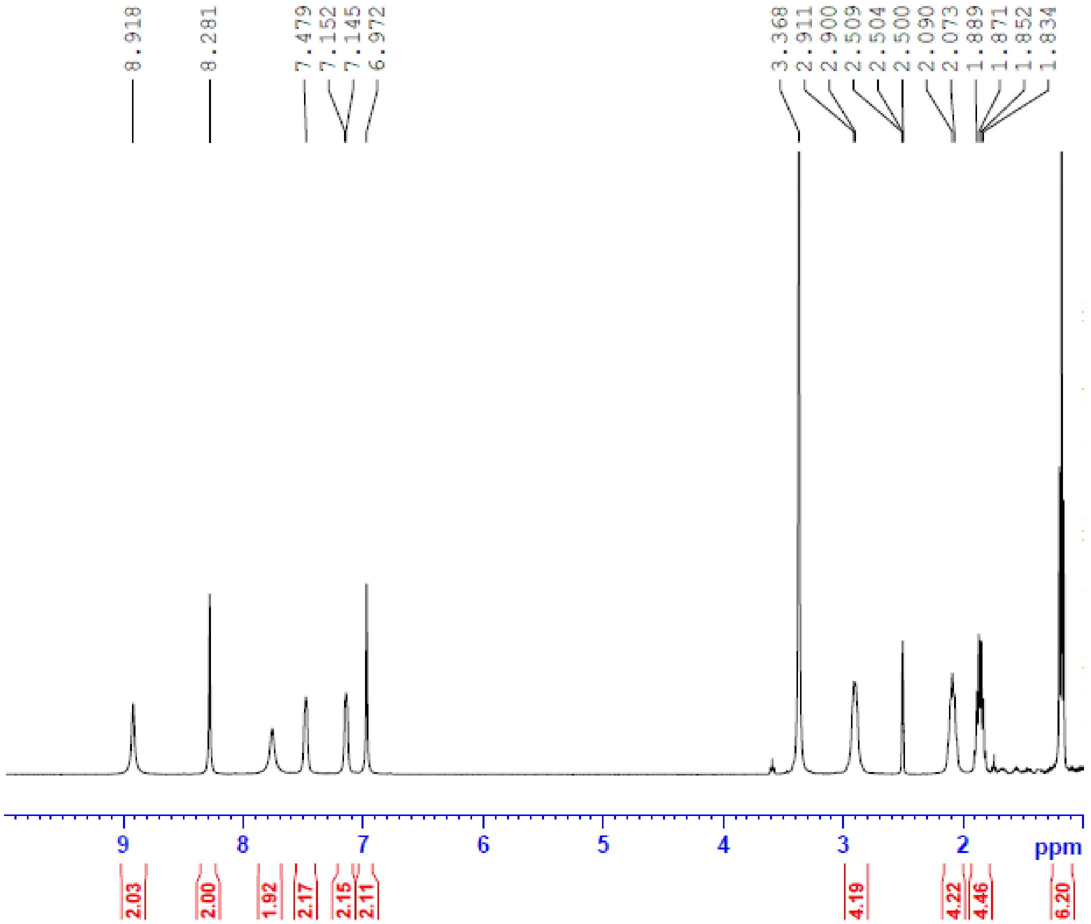

Figure S6. ^{1}H-NMR spectrum (DMSO-d6) for A-B monomer **(8)**

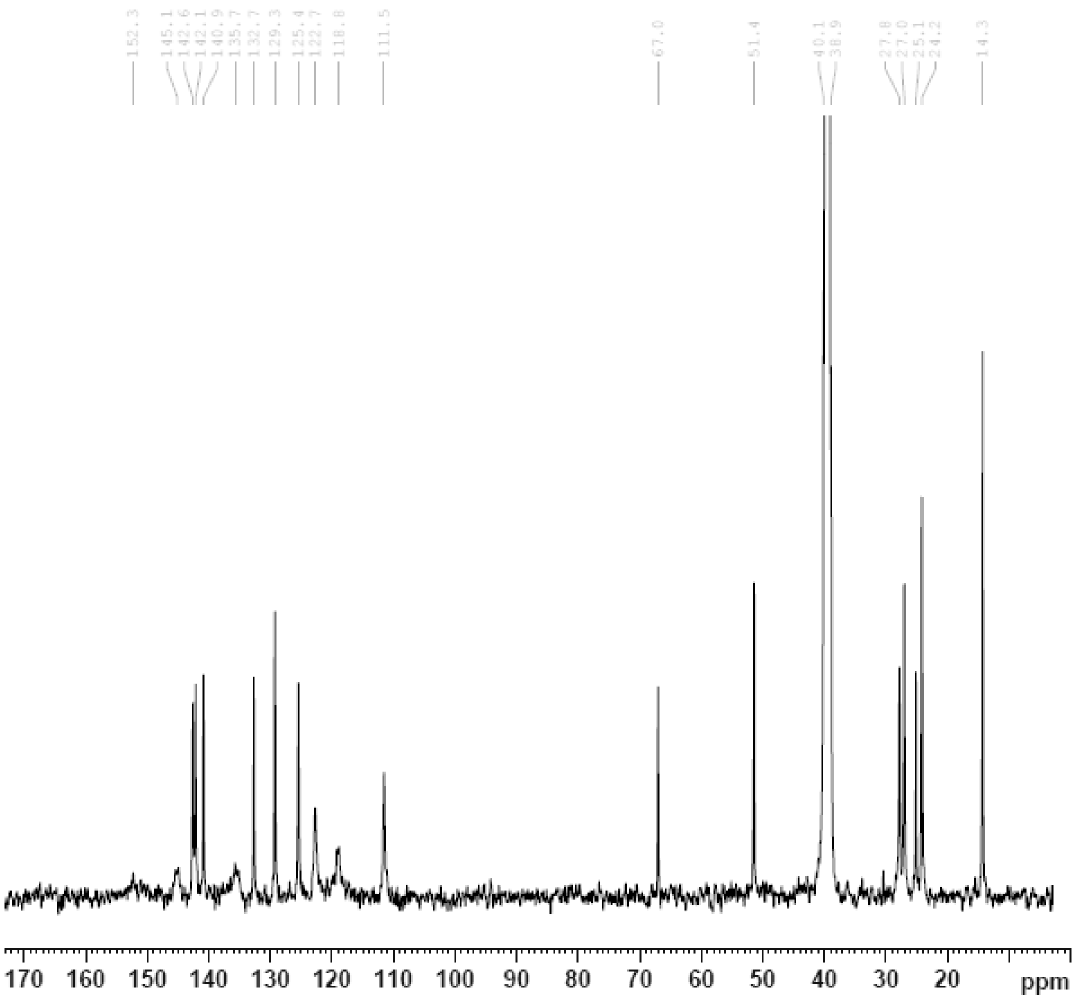

Figure S7. ^{13}C-NMR spectrum (DMSO-d6) for A-B monomer **(8)**

3. Preparation of the model compound 9.

To a dry one-neck, round-bottom flask equipped with nitrogen inlet and magnetic stirrer and flushed with nitrogen gas was added catechol (0.059 g, 0.53 mmol), compound **7** (0.30 g, 0.52 mmol) and anhydrous DMF (10 ml). To this stirred mixture, (0.21 g, 1.45 mmole) of finely powder of anhydrous potassium carbonate was added. The reaction mixture was heated at 140 ^{o}C for 3 hours. On cooling, the reaction mixture was added to distilled water (200 ml) and the crude product was filtered, washed with distilled water and dried to give yellow powder (0.29 g, 91 % yield). Purification by column chromatography using (silica gel) and DCM as an eluent afforded yellow solid. M.P = 249-250 ^{o}C. Elemental Analysis; (Found C, 79.03; H, 6.11; N, 4.39. Calc. for $C_{42}H_{38}N_2O_4$: C, 79.47; H, 6.03; N, 4.41%). ^{1}H-NMR (400 MHz; $CDCl_3$) δ (ppm): 1.22 (t, *J* = 7.6 Hz, 6 H), 1.90 (sixt, *J* = 7.2 Hz, 4H), 2.18-2.33 (br m, 4H), 3.11-2.95 (br m, 4H), 3.87 (s, 6H), 6.90-6.82 (m, 2H), 6.98-6.91 (m, 2H), 7.08 (s, 2H), 7.17-7.10 (m, 2H), 7.46 (s, 4H), 7.55-7.48 (m, 2H), 7.85 (br s, 2H); ^{13}C-NMR (100 MHz; $CDCl_3$) δ (ppm): 14.3, 25.0, 27.6, 28.5, 52.3, 56.3, 107.9, 111.6, 116.6, 119.7, 119.9, 120.1, 122.7, 123.3, 124.3, 125.5, 140.5, 141.7, 141.9, 145.2, 146.5.

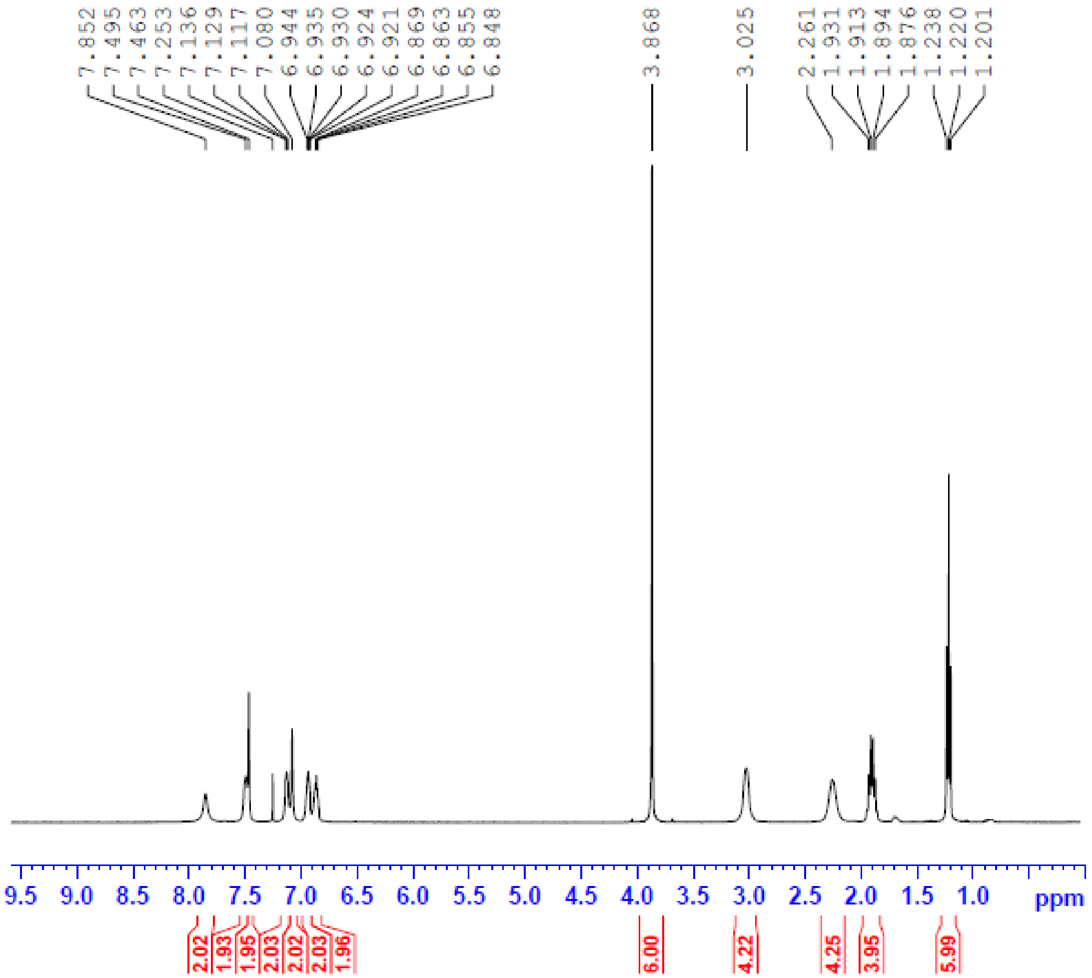

Figure S8. ^{1}H-NMR spectrum ($CDCl_3$) for model compound **(9)**

4. Self-polymerization of A-B monomer 8.

To a stirred solution of monomer **8** (0.56 g, 0.98 mmol) and 18-crown-6 (0.26 g, 0.98 mmol) in anhydrous DMF (10 ml) was added anhydrous potassium carbonate (3 mmol). The mixture was heated to 150 ^{o}C under a nitrogen atmosphere for 5 hours. On cooling, the reaction mixture was poured into distilled water and the crude product was collected by filtration, washed with distilled water and methanol and then dried to afford an orange powder. Purification of the crude polymer was achieved by reprecipitation from chloroform solution into methanol. This procedure was repeated twice. The resulting solid was filtered, dried and ground to give a yellow-orange powder (0.42 g, 86 %). Elemental Analysis; (Found C, 78.69; H, 5.24; N, 5.41. Calc. for $C_{34}H_{28}N_2O_2$ (repeat unit, 82.23; H, 5.68; N, 5.64 %). ^{1}H-NMR (400 MHz; $CDCl_3$) δ (ppm): 1.14 (br t, 6H), 1.81(br m, 4H), 2.14 (br m, 4H), 2.90 (br, 4H), 7.07 (br s, 4H), 7.36 (br m, 4H), 7.81 (br m, 2H); IR (KBr, cm^{-1}): 1280 & 1290 (C-O), 1420, 1456, 1610, 2870-2953 (aliph. CH), 3065 (arom.CH). Analysis by GPC ($CHCl_3$, polystyrene standard): *M*n = 30000, *M*w = 56000 g mol^{-1}, polydispersity PDI = 1.9; surface area (BET) = 523 m^{2}g^{-1}, total pore volume = 0.42 cm^3 g^{-1} at (P/Po = 0.98, adsorption); TGA analysis (Nitrogen): Initial weight loss due to thermal degradation commences at ~ 460 °C, .

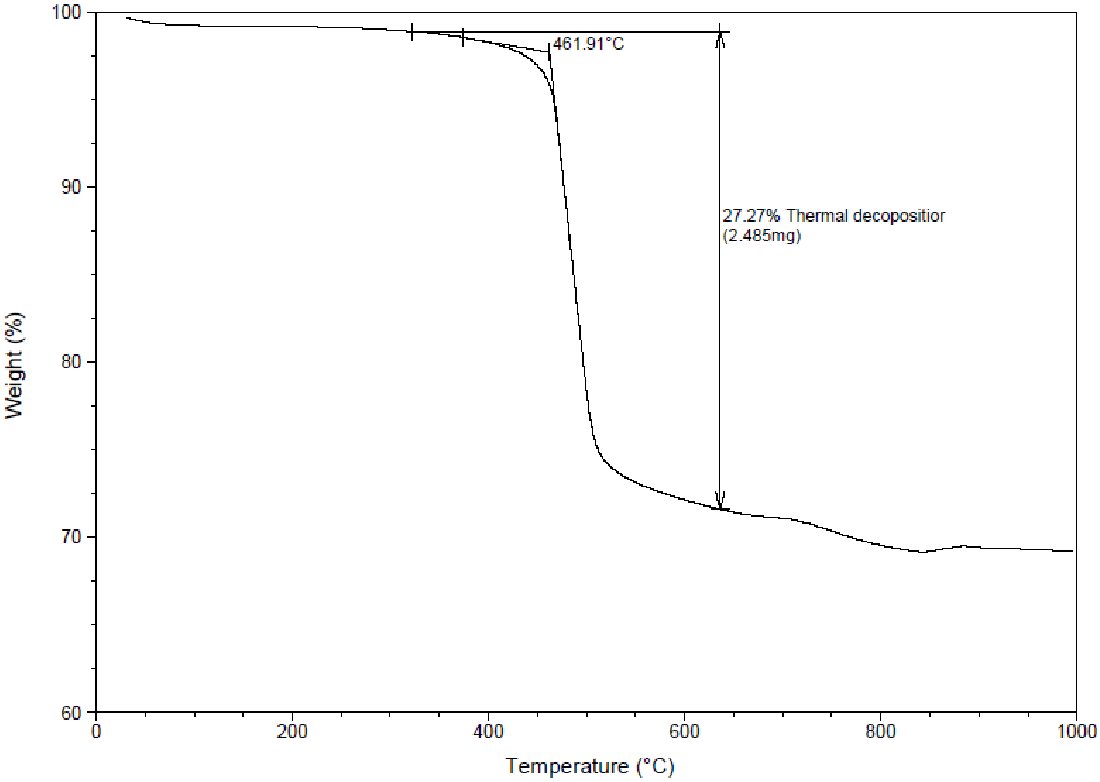

Figure S9. ^{1}H-NMR spectrum ($CDCl_3$) for the polymer**.**

ESI References

1. B. S. Ghanem, N. B. McKeown, P. M. Budd, and D. Fritsch, *Macromolecules*. 2008, **41**, 1640.

2. Q. S. Zong and C.-F. Chen, *Org. Lett.* 2006, **8**, 211.

3. J.-M. Zhao, H.-Y. Lu, J. Cao and C.-F. Chen, *Tetrahedron Lett.* 2009, **50**, 219