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Polyurethanes Containing Indole-Based Nonlinear Optical Chromophores: From Linear Chromophore to H-Type

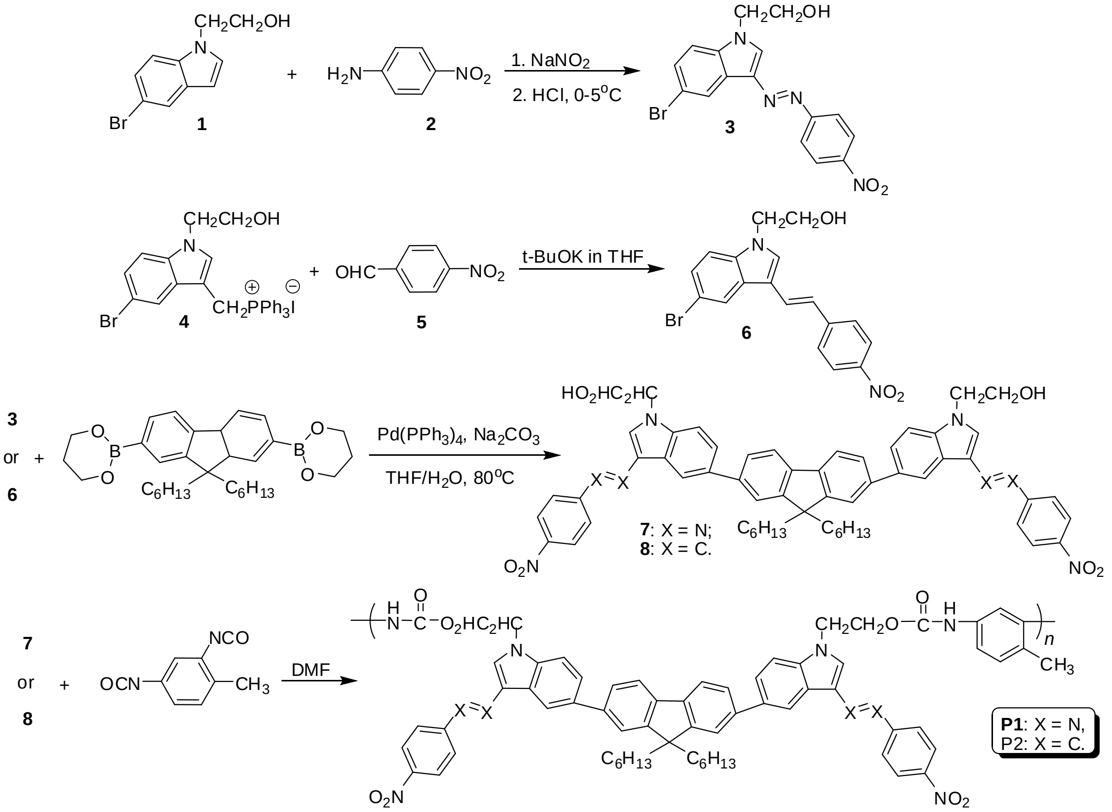
Qianqian Li,[1] Gui Yu,[2] Jing Huang,[1] Haijie Liu,[1] Zhen Li,*[1] Cheng Ye,[2] Yunqi Liu,[2] Jingui Qin[1]

[1] Department of Chemistry, Wuhan University, Wuhan 430072, China

Fax: 86-27-68756757; E-mail: lizhen@whu.edu.cn

[2] Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, China

Scheme 1



Experimental Section

Materials and Instrumentations

Tetrahydrofuran (THF) was dried over and distilled from a K-Na alloy under an atmosphere of dry nitrogen. 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) was purchased from Aldrich. All other reagents were used as received. **1** and **4** were prepared following the similar procedure as we reported previously.[1]

^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury300 spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000-400 cm^{-1}. UV-visible spectra were obtained using a Schimadzu UV-2550 spectrometer. EI-MS spectra were recorded with a Finnigan PRACE mass spectrometer. Elemental analyses were performed by a CARLOERBA-1106 micro-elemental analyzer. The thermometer for measurement of the melting point was uncorrected. The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

Synthesis of compound 3

2 (0.61g, 4.4 mmol) was dissolved in a water solution of 35% hydrochloric acid. The mixture was cooled to 0-5 °C in an ice bath, and then a solution of sodium nitrite (0.33 g, 4.8 mmol) in water was added dropwise to the above solution with stirring. After stirred below 5 °C for 15 min, a solution of **1** (0.96 g, 4.0 mmol**)** in ethanol (15 mL) was added slowly. The mixture was 1eft in the ice bath for another 1 h, and some sodium bicarbonate was added to adjust the pH value to 7.0. The red precipitate was filtered, washed with water, and dried in a vacuum desiccator. The crude product was purified with column chromatography on silica gel using petroleum/ethyl acetate (1/3) as eluent to afford a red solid **3** (0.90 g, 57.8 %). ^{1}H NMR ($CDCl_3$) δ (ppm): 8.67 (s, 1H, ArH), 8.33 (d, 2H, *J* = 8.7 Hz, ArH), 8.12 (s, 1H, ArH), 7.95(d, 2H, *J* = 8.7 Hz, ArH), 7.47 (d, 1H, *J* = 8.7 Hz, ArH), 7.30 (d, 1H, *J* = 8.7 Hz, ArH), 4.39 (t, 2H, *J* = 4.2 Hz, -O-CH_2-), 4.09 (br, 1H, -N-CH_2-). ^{13}C NMR (aceton-d_6) δ (ppm): 157.7, 147.4, 140.0, 136.5, 135.2, 127.1, 125.3, 124.9, 122.3, 120.5, 116.6, 113.1, 60.6, 49.9. MS (EI), *m/z* $[M+2]^+$:390.1, calcd, 388.0.

Synthesis of compound 6:

4 (2.83 g, 4.40 mmol) was suspended in 10 mL of THF under nitrogen. *t*-BuOK (1.34 g, 12.0 mmol) was added directly as a solid and the resultant mixture was stirred at room temperature for 10 min. After the addition of the solution of **5** (0.60 g, 4.00 mmol) in THF (20 mL) dropwise, the resultant mixture was stirred at room temperature overnight, then poured into 100 mL of water. The organic product was extracted with chloroform, and dried over anhydrous Na_2SO_4. After removing the solvent, the crude product was purified through a silica gel chromatography column by using petroleum/ethyl acetate (1/3) as eluent to afford a red solid **6** (0.74 g, 43.4 %). ^{1}H NMR ($CDCl_3$) δ (ppm): 8.20 (d, 2H, *J* = 8.1 Hz, ArH), 8.08 (s, 1H, ArH), 7.68-7.52 (m, 4H, ArH and -CH=CH-), 7.46-7.29 (m, 2H, ArH), 7.05 (d, 1H, *J* = 16.8 Hz, -CH=CH-), 4.28 (t, 2H, *J* = 4.5 Hz, -O-CH_2-), 3.99 (t, 2H, *J* = 4.2 Hz, -N-CH_2-). ^{13}C NMR (aceton-d_6) δ (ppm):146.1, 145.9, 136.5, 132.2, 132.1, 132.0, 128.9, 128.8, 128.1, 126.6, 126.2, 125.0, 124.1, 122.6, 122.1, 113.6, 113.1, 112.6, 61.0, 49.3. MS (EI), *m/z* [M^+]:386.0, calcd, 386.0.

Synthesis of compound 7, 8

A mixture of **3** (0.25 g, 0.63 mmol), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (0.15 g, 0.30 mmol), sodium carbonate (0.64 g, 6.0 mmol), and a catalytic amount of tetrakis(triphenylphosphine) palladium $Pd(PPh_3)_4$ was carefully degassed and charged with nitrogen. Subsequently THF (18 ml) and deoxidized water (9 ml) were added by syringe. The reaction mixture was stirred at 80 °C for 36 h. After it was cooled to room temperature, the organic layer was separated, dried over sodium sulfate, and evaporated to dryness. The crude product was purified by column chromatography on silica gel using petroleum/ethyl acetate (1/3) as eluent to afford a red solid **7** (0.15 g, 54.6 %). Mp = 181–183 °C. IR (thin film), υ (cm^{-1}): 1593 (-C=C-), 1522, 1330 (-NO_2). ^{1}H NMR (DMSO-d_6) δ (ppm): 8.77 (s, 2H, ArH), 8.61 (s, 2H, ArH), 8.39 (d, *J* = 9.0 Hz, 4H, ArH), 8.00 (d, *J* = 9.3 Hz, 4H, ArH), 7.96 (d, *J* = 7.5 Hz, 2H, ArH), 7.83-7.71 (m, 8H, ArH), 4.46 (br, 4H, -O-CH_2-), 3.87 (t, *J* = 5.1 Hz, 4H, -N-CH_2-), 2.15 (br, 4H, -CH_2-), 1.06 (br, 16H, -CH_2-), 0.67 (br, 6H, -CH_3). ^{13}C NMR (DMSO-d_6) δ (ppm): 157.9, 152.0, 147.1, 140.7, 140.0, 137.5, 137.3, 136.4, 128.7, 127.1, 126.7, 125.6, 124.4, 122.5, 122.1, 121.5, 121.0, 119.9, 112.4, 60.4, 55.6, 50.0, 31.5, 31.1, 29.7, 24.2, 22.6, 14.4. Anal. Calcd for: $C_{57}H_{58}N_8O_6$: C, 71.98; H, 6.15; N, 11.78; Found: C, 71.58; H, 6.23; N, 11.28. UV-Vis (THF, 1.07 $\times 10^{-5}$ mol/L), λ_{max} = 432 nm; ε_{max} = 4.7×10^4 mol^{-1} L cm^{-1}, MS (EI), *m/z* [M+1]$^+$: 951.0, calcd, 950.5.

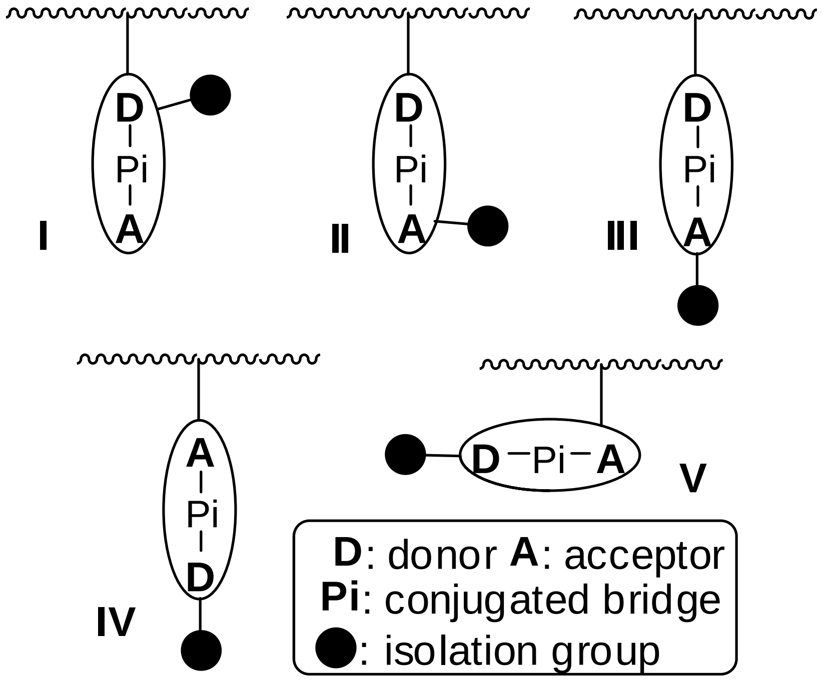
Following the similar procedure, **compound 8** was prepared. The crude product was purified by column chromatography on silica gel using petroleum/ethyl acetate (1/3) as eluent to afford a red solid (0.25 g, 22.9 %). Mp = 106–108 °C. IR (thin film), υ (cm^{-1}): 1588 (-C=C-), 1533, 1333 (-NO_2). ^{1}H NMR ($CDCl_3$) δ (ppm): 8.20 (d, *J* = 8.7 Hz, 6H, ArH), 7.85 (d, *J* = 8.4 Hz, 2H, ArH), 7.70 (d, *J* = 7.8 Hz, 2H, ArH), 7.65-7.58 (m, 10H, ArH and -CH=CH-), 7.51 (d, *J* = 7.2 Hz, 4H, ArH), 7.19 (d, *J* = 16.8 Hz, 2H, -CH=CH-), 4.37 (t, *J* = 4.2 Hz, 4H, -O-CH_2-), 4.06 (br, 4H, -N-CH_2-), 2.09 (br, 4H, -CH_2-), 1.10 (br, 16H, -CH_2-), 0.75 (t, *J* = 4.0 Hz, 6H, -CH_3). ^{13}C NMR ($CDCl_3$) δ (ppm): 152.0, 146.1, 145.6, 141.3, 139.9, 137.0, 135.5, 130.5, 130.0, 127.1, 126.7, 126.5, 126.0, 125.8, 124.5, 123.9, 123.1, 122.7, 122.2, 121.7, 120.2, 119.1, 114.5, 110.5, 62.0, 55.5, 49.2, 40.7, 31.7, 31.1, 30.6, 30.0, 24.1, 22.8, 14.3. Anal. Calcd for: $C_{61}H_{62}N_4O_6$: C, 77.35; H, 6.60; N, 5.92; Found: C, 77.64; H, 7.13; N, 5.64. UV-Vis (THF, 1.08 $\times 10^{-5}$ mol/L), λ_{max} = 427 nm; ε_{max} = 2.2×10^4 mol^{-1} L cm^{-1}, MS (EI), *m/z* [M+1]$^+$: 947.5, calcd, 946.5.

Preparation of Polymer Thin Films. The polymers were dissolved in THF (concentration ~4 wt %) and the solutions were filtered through syringe filters. Polymer films were spin coated onto indium-tin-oxide (ITO)-coated glass substrates, which were cleaned by *N*, *N*-dimethyformide, acetone, distilled water and THF sequentially in ultrasonic bath before use. Residual solvent was removed by heating the films in a vacuum oven at 40 °C.

NLO Measurement of Poled Films. The second-order optical nonlinearity of the polymers was determined by in-situ second harmonic generation (SHG) experiment using a closed temperature-controlled oven with optical windows and three needle electrodes. The films were kept at 45° to the incident beam and poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows: temperature: different for each polymer (Table 1 in the main text); voltage: 7.5 kV at the needle point; gap distance: 0.8 cm. The SHG measurements were carried out with a Nd:YAG laser operating at a 10 Hz repetition rate and an 8 ns pulse width at 1064 nm. A Y-cut quartz crystal served as the reference.

[1] [1a] Z. Li, C. Huang, J. Hua, J. Qin, Z. Yang, C. Ye, *Macromolecules* **2004**, *37*, 371; [8b] Q. Li, Z. Zhu, Z. Li, J. Qin, *Chin. J. Chem.* **2007**, *25*, 1409; [8c] Z. Li, Jingui Qin, S. Li, C. Ye, J. Luo, Y. Cao, *Macromolecules* **2002**, *35*, 9232.

Chart S1



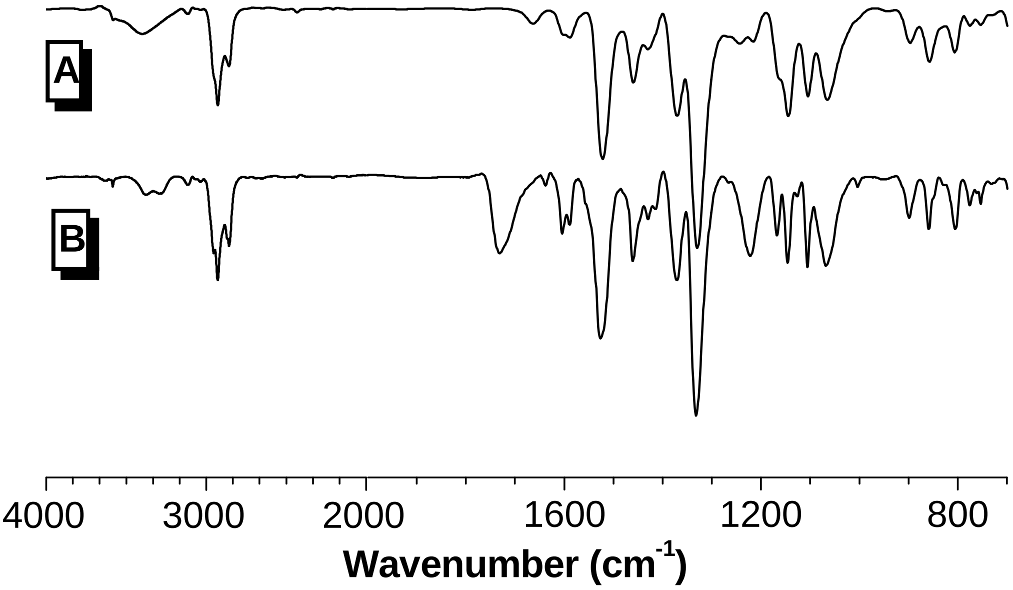


Figure S1. IR spectrum of chromophore **7** (A) and polymer **P1** (B).

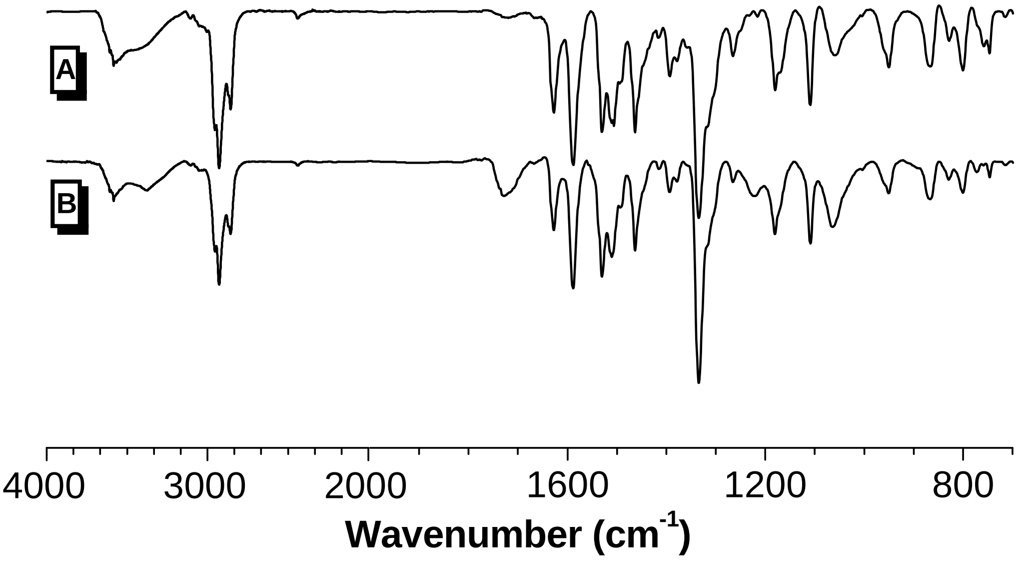


Figure S2. IR spectrum of chromophore **8** (A) and polymer **P2** (B).

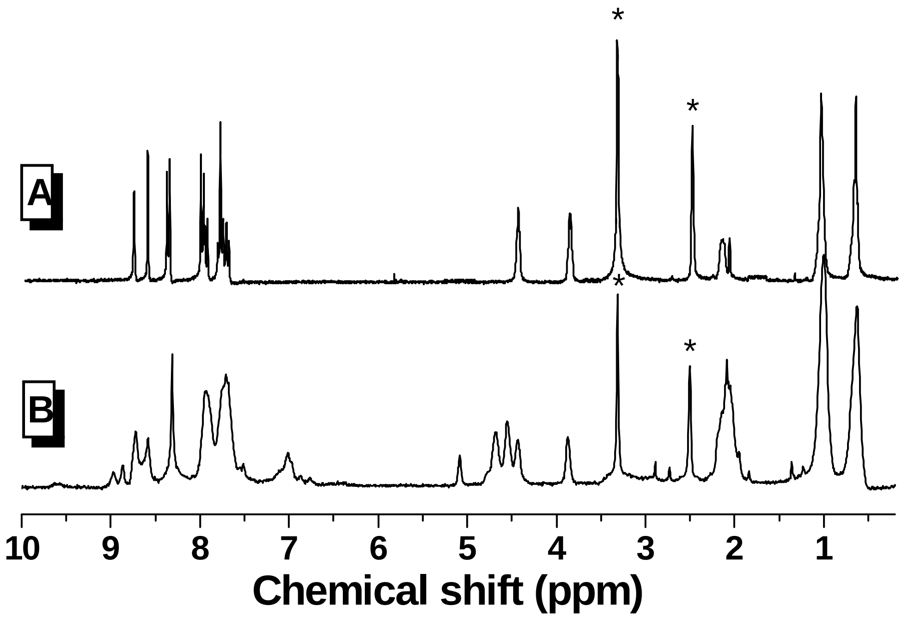


Figure S3. ^{1}H NMR spectra of chromophore **7** (A) and **P1** (B) in DMSO-d_6. The solvent peaks are marked with asterisks (*).

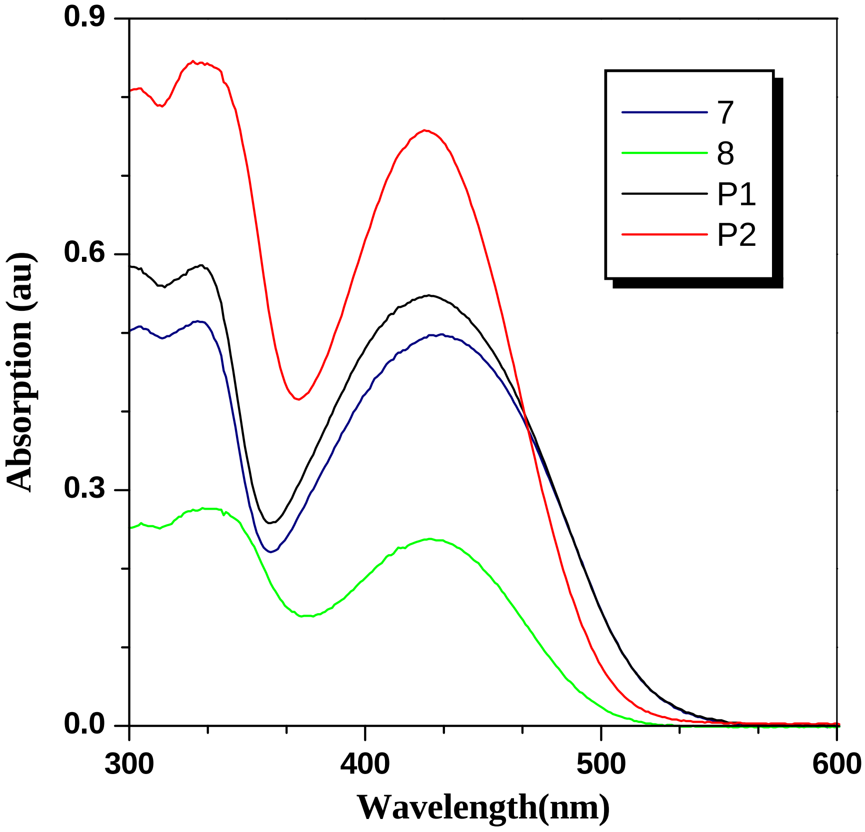
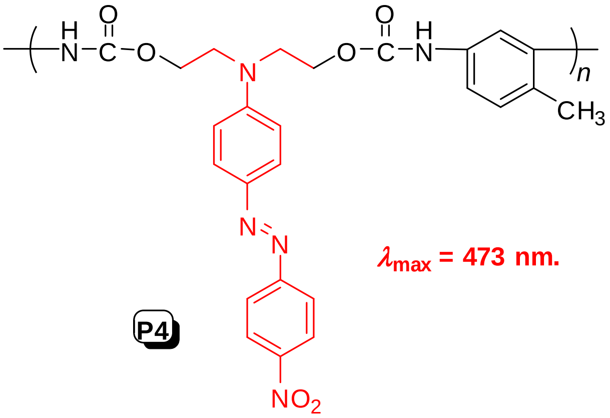


Figure S4. UV-Vis spectra of THF solutions of Chromophore **7** and **8**, **P1** and **P2**. Concentration: 0.02 mg/mL.

Chart S2



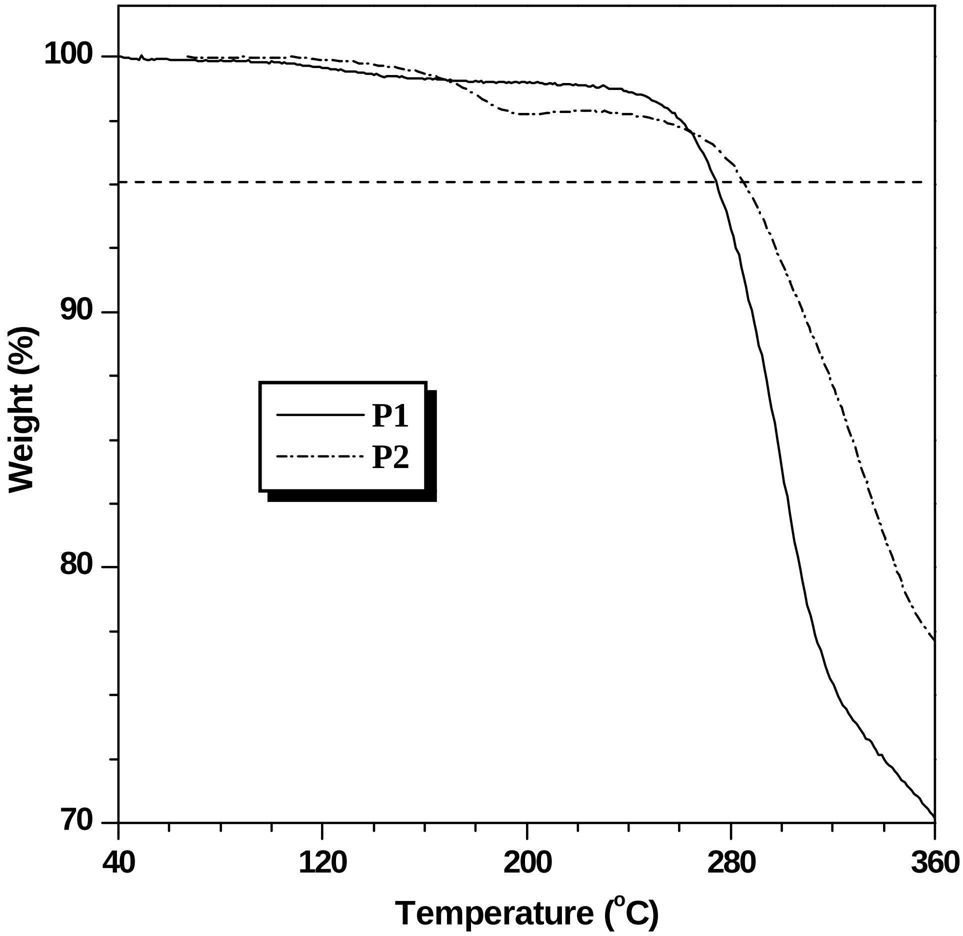
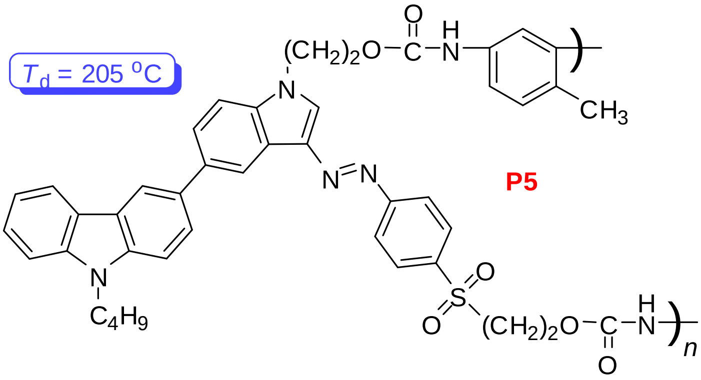


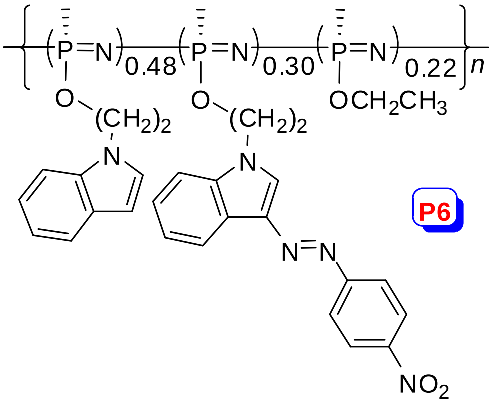
Figure S5. TGA thermograms of **P1** and **P2** measured in argon at a heating rate of 10 °C/min.

Chart S3


T_d = 205 ^oC

P5

Chart S4


P6