# Supporting Information

## Topochemical Polymerization of Unsymmetrical Aryldiacetylenes Supramolecule with Nitrophenyl Substituents Utilizing C–H···π Interactions

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## General

Reagents were obtained from commercial sources and were used as received. Solvents were distilled from appropriate drying agents under nitrogen and all reactions were run under dry nitrogen. Carbon, hydrogen and nitrogen analyses were performed by a

commercial service and were satisfactory for all compounds. All $^{1}H$ spectra were acquired at 400MHz. All $^{13}C$ NMR spectra were acquired at 75MHz. In all cases, deuterated chloroform ($CDCl_3$) was used as the solvent. Mass spectral data were acquired on a GC/MS system. IR spectrum was measured with Infrared spectrometer (Bruker VECTOR, German). Raman spectra were measured on FT-185 Infrared and Raman spectroscopy. UV spectra were carried on Lambda 35 UV-Visible (Perkin-Elmer Inc. USA). FL was measured on FluoroMax-P (Jobin Yvon Inc. USA) spectrophotometer. Water contact angles were carried out on HARKE-SPCAX1 with which a CAMERAY digital color CCD camera was used for the measurement of the contact angle of water droplets on the surface of **4b** cast film irradiated by UV light. Crystal structure was measured on an XPert PRO (PANalytical). Deep UV irradiation was carried out with EX250 UV light source (Honya-Schott Ltd., Japan). Optical microscopies were observed by microscope (OLYMPUS BX51, OLYMPUS Co., Japan). The electrochemical performances were measured on a CHI660E electrochemical workstation at room temperature. Gel permeation chromatography was made on PL GPC 50 (Polymer Lab, UK). Polymer solution in tetrahydrofunan (1% w/v) was prepared, and then filtrated over 0.2μm filters.

Table S1 Gel permeation chromatography analysis of yellow soluble oligomers **poly-4a** and **poly-4b**. (M: monomer molecular weight; Mn: Number-average Molecular Weight; Mw: Weight-average Molecular Weight; D: Molecular weight distribution index)

| Sample | M | Mn | Mw | D |
|---|---|---|---|---|
| **Poly-4a** | 215 | 825 | 852 | 1.03 |
| **Poly-4b-1** | 215 | 14293 | 15203 | 1.06 |
| **Poly-4b-2** | 215 | 1572 | 1617 | 1.03 |

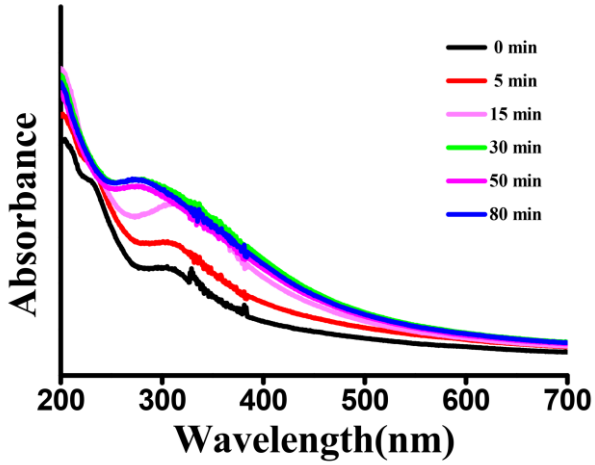



Figure S1 UV-vis spectrum of **4a** cast film on quartz substrate as a function of UV irradiation time at 250nm

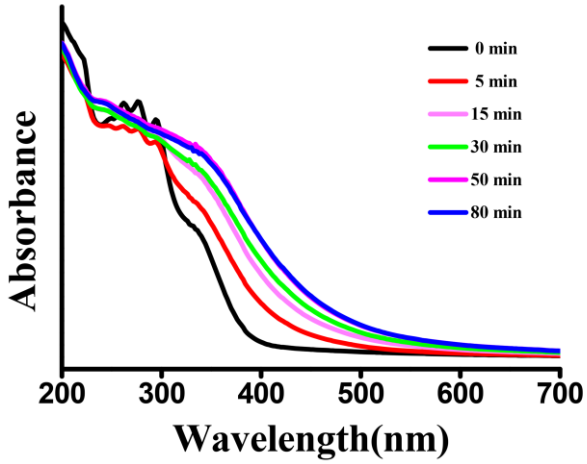



Figure S2 UV-vis spectrum of **4b** cast film without vacuuming on quartz substrate as a function of UV irradiation time at 250nm.

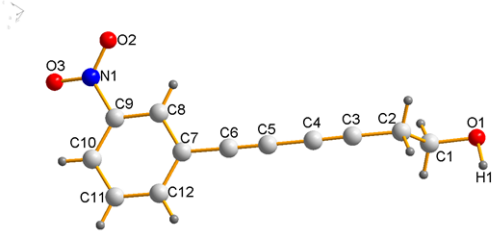



Figure S3. Perspective view with partial atom-labeling scheme of **4b**. Hydrogen atoms are omitted for clarity.

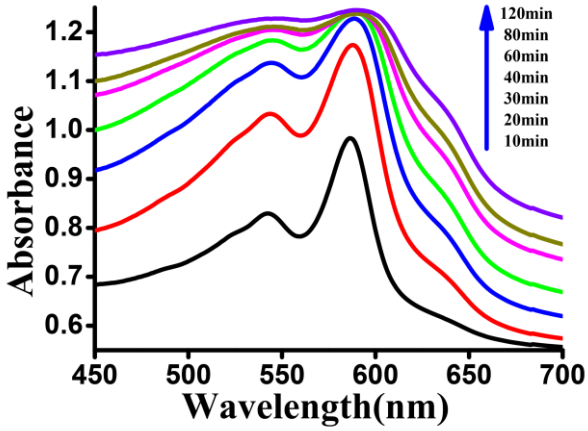



Figure S4 UV-vis spectrum of **4b** cast film on quartz substrate as a function of UV irradiation time at 365nm.

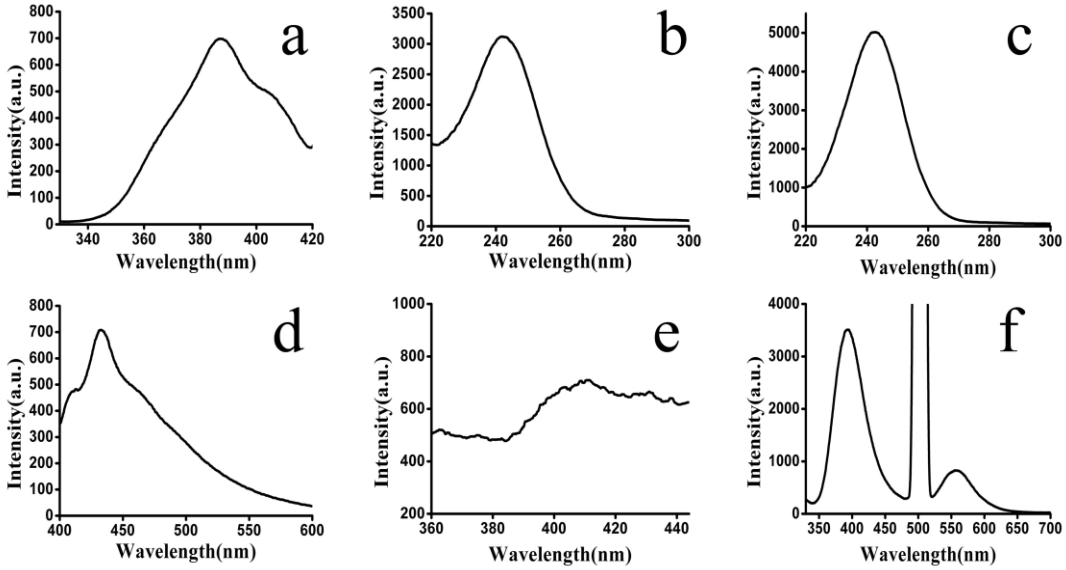
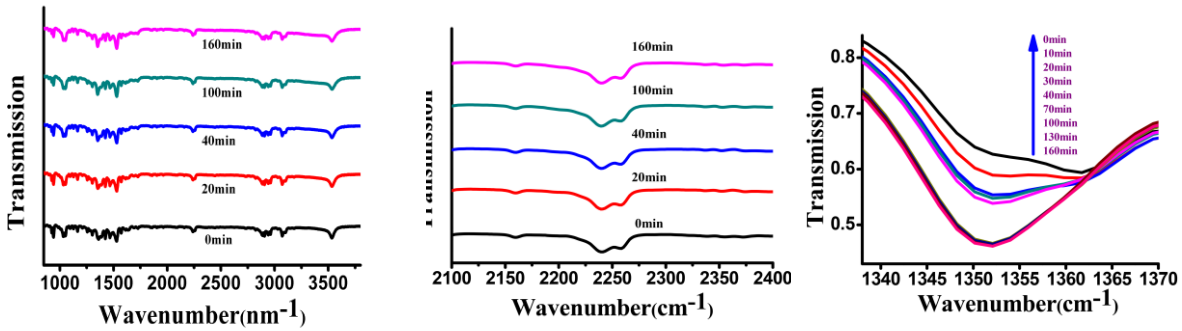



Figure S5 Fluorescence excitation (a, b, c) and emission (d, e, f) spectra of **4b**: (a, d) solution; (b, e) cast film and (c, f) cast film irradiated at 250nm.




a b c

Figure S6 Infrared spectra of **4b** cast film on $CaF_2$ substrate at different irradiation time (a), stretching vibration of acetylene and triple bond (b) and changes of symmetric -$NO_2$ stretching (c).

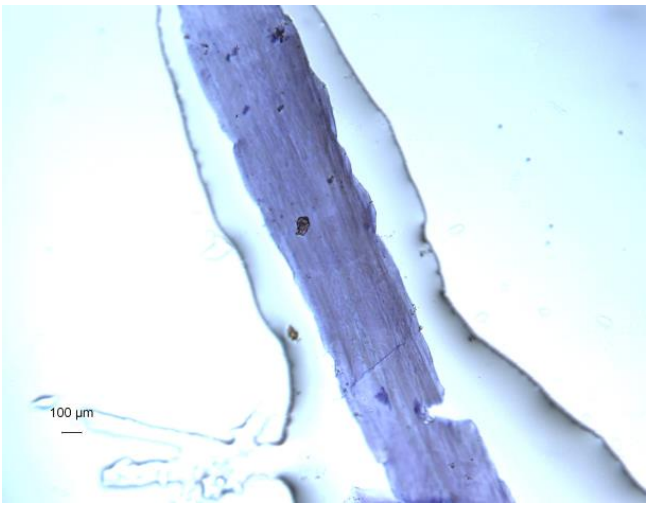



Figure S7 The change of **4b** crystal heated.

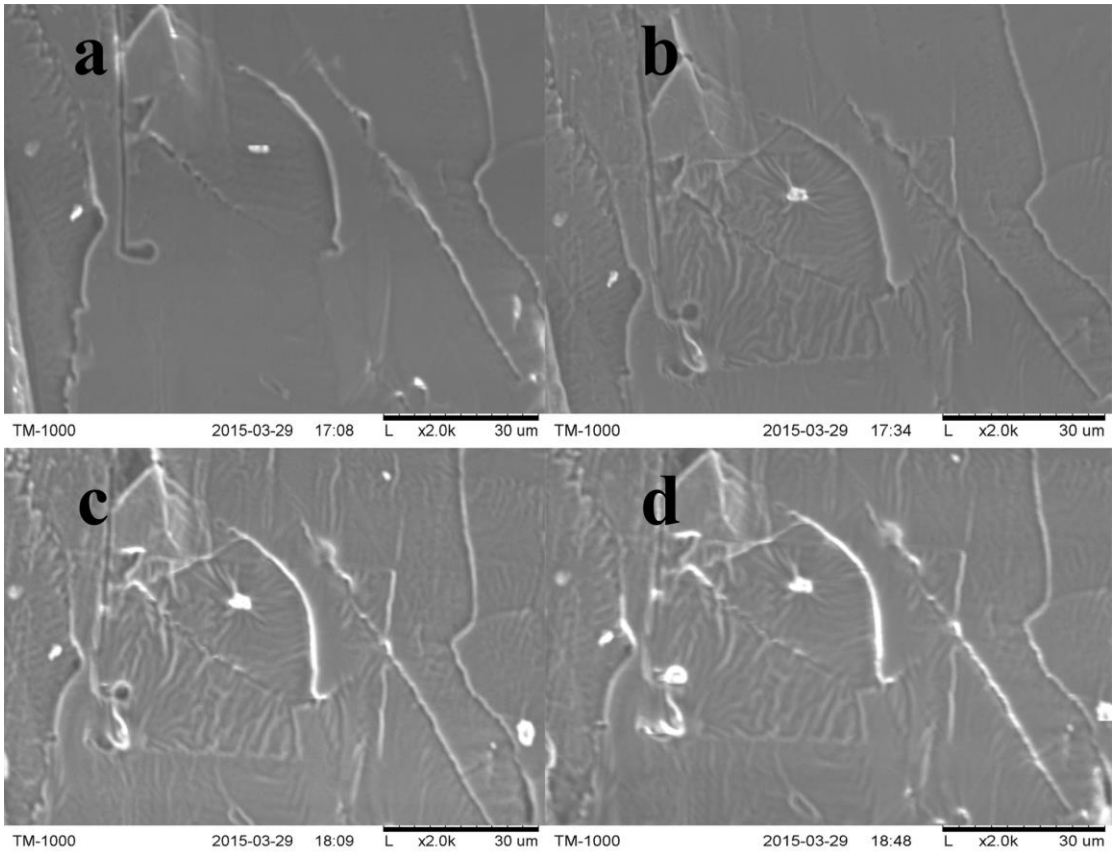



Figure S8 SEM images of **4b** cast film irradiated at different time. (a), 0min;(b), 20min;(c), 40min;(d), 60min.

Table S2 Summary of System Resistances ($R_1$) and Charge Transfer Resistances ($R_2$) of **4b** crystal before (**4b**) and after UV irradiation (**P-4b**).

| Sample | $R_1(\Omega)$ | $R_2(\Omega)$ |
|---|---|---|
| **4b** | 5.953 | 10.62 |
| **P-4b** | 4.245 | 9.654 |

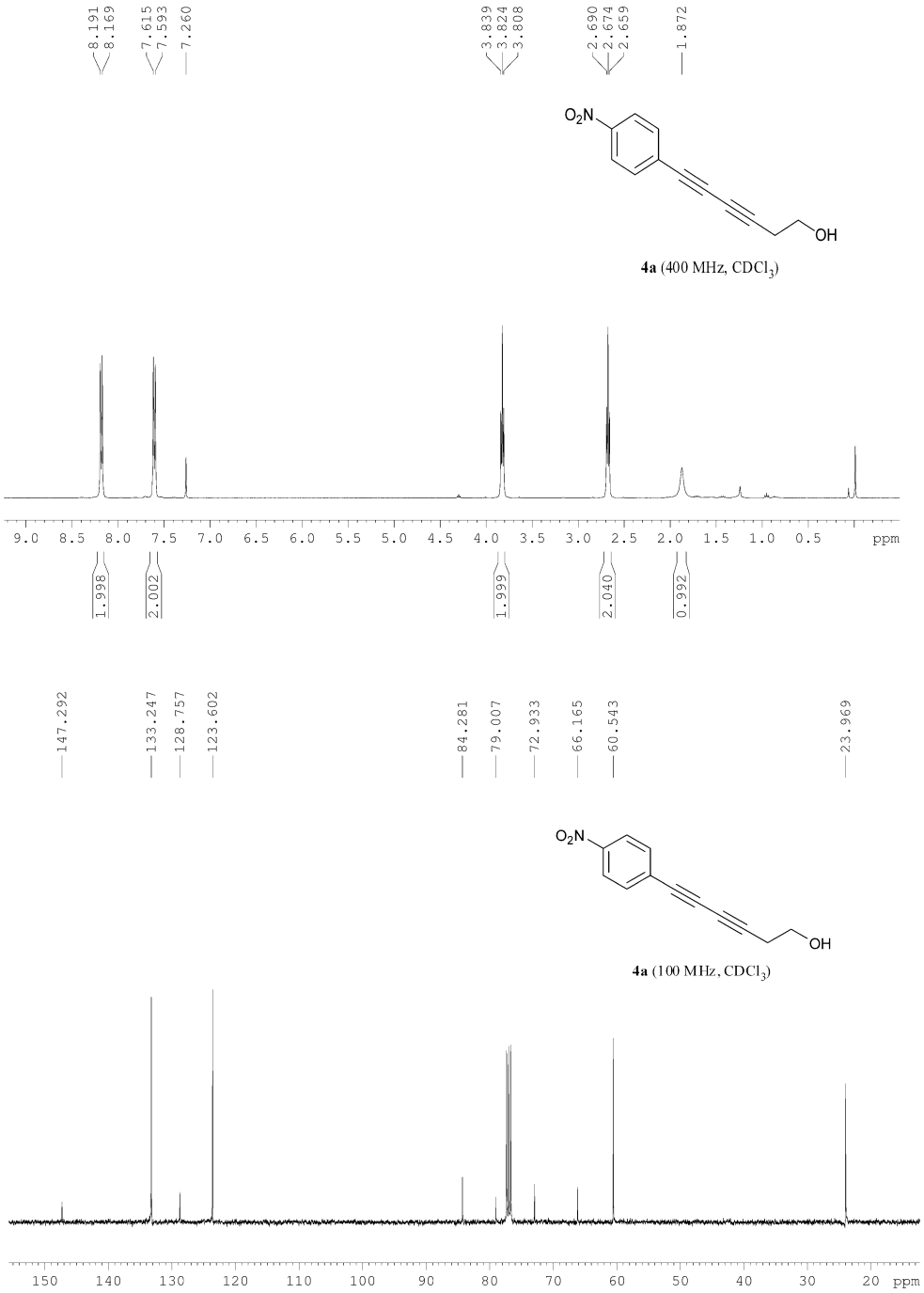



Figure S9 $^{1}H$ and $^{13}C$ NMR Spectra of **4a.**

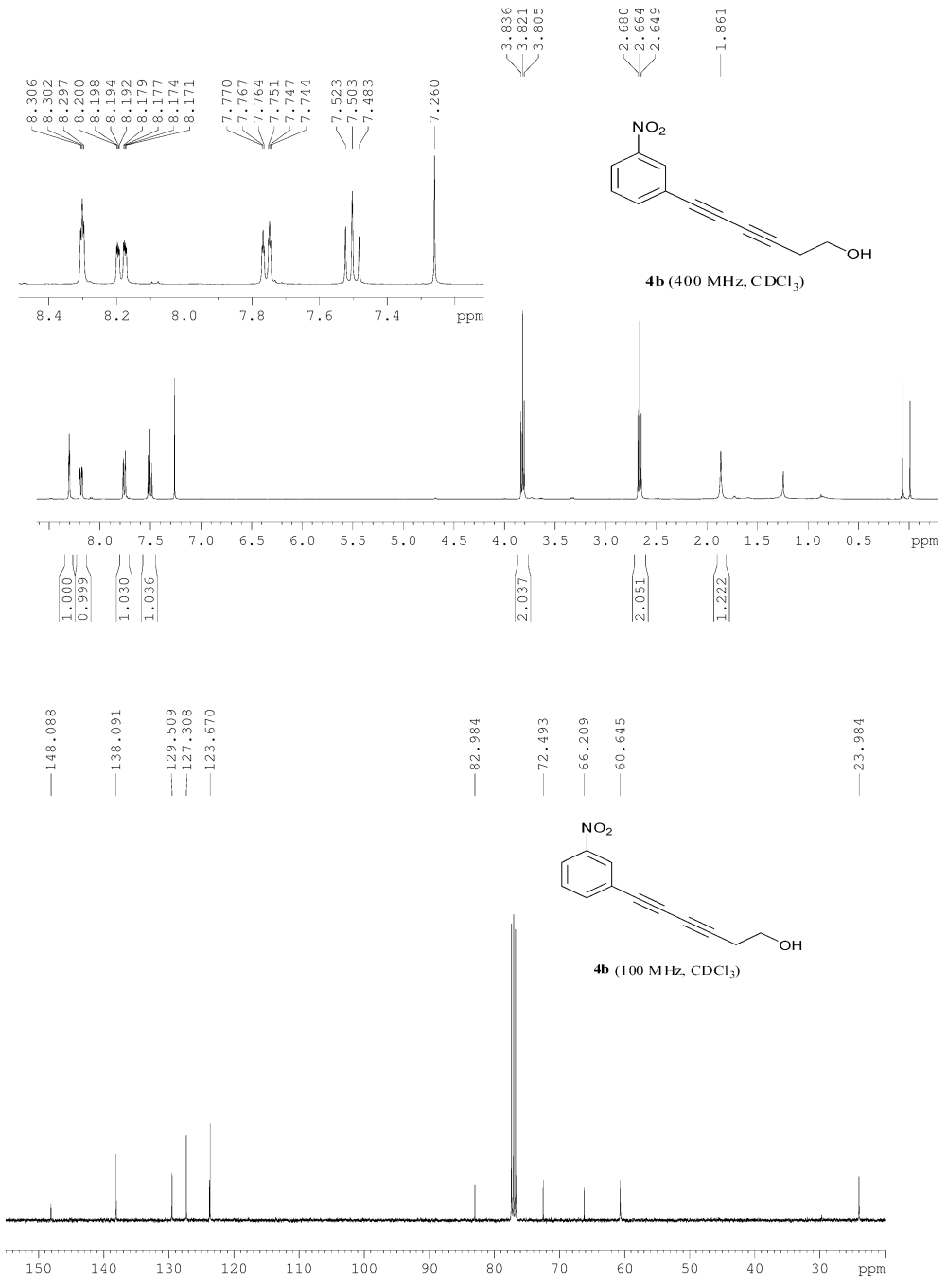



Figure S10 $^{1}H$ and $^{13}C$ NMR Spectra of **4b.**