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Supplementary Information

Steric Hindrance Effect on Thermo- and Photo- responsive Properties of Pyrene Based Polymers

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Instruments and measurements

Nuclear magnetic resonance (NMR). ^1H and ^{13}C NMR spectroscopy were performed on a Bruker ARX400 MHz spectrometer using tetramethylsilane (TMS) as the internal standard at ambient temperature. The chemical shifts are reported on the ppm scale.

10 Gel permeation chromatography (GPC). The apparent number average molecular weight (M_n) and polydispersity index ($\text{PDI} = M_w/M_n$) were measured on a GPC (WATERS 1515) instrument with a set of HT3, HT4 and HT5 columns. The μ -styragel columns used THF as an eluent and the flow rate was 1.0 mL min^{-1} at $38 \text{ }^\circ\text{C}$. All the GPC data were calibrated with polystyrene standards.

Thermogravimetric analysis (TGA). TGA was performed on a TA SDT 2960 instrument at a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$ in a nitrogen atmosphere.

15 Differential scanning calorimetry (DSC). DSC traces of the polymer were obtained using a TA Q10 DSC instrument. The temperature and heat flow were calibrated using standard materials (indium and zinc) at cooling and heating rates of $10 \text{ }^\circ\text{C min}^{-1}$. The sample, with a typical mass of about 5 mg, was encapsulated in sealed aluminum pans.

Ultraviolet-visible spectra (UV-Vis). UV-Vis absorption spectra were recorded on an Agilent Cary600 spectrometer.

20 Cloud point temperature (T_c). The polymer solutions were prepared by directly mixing and stirring at temperatures below the respective cloud point temperature (T_c) in THF, and then placed in a quartz cell with a path length of 1.0 cm. The transmittances of the solutions were collected at a wavelength of 800 nm. DI-THF at $25 \text{ }^\circ\text{C}$ was set to be 100% of transmittance. T_c was determined at 50% of transmittance in the heating cycle with the heating rates of $1 \text{ }^\circ\text{C min}^{-1}$.

Photoluminescence (PL). PL spectra were recorded on a Hitachi-hightech F-4600 spectrofluorometer.

The photodegradation of the polymers was obtained by using a 365 nm UV LED (FUWO, FUV-6BK, 60 mW/cm^2)

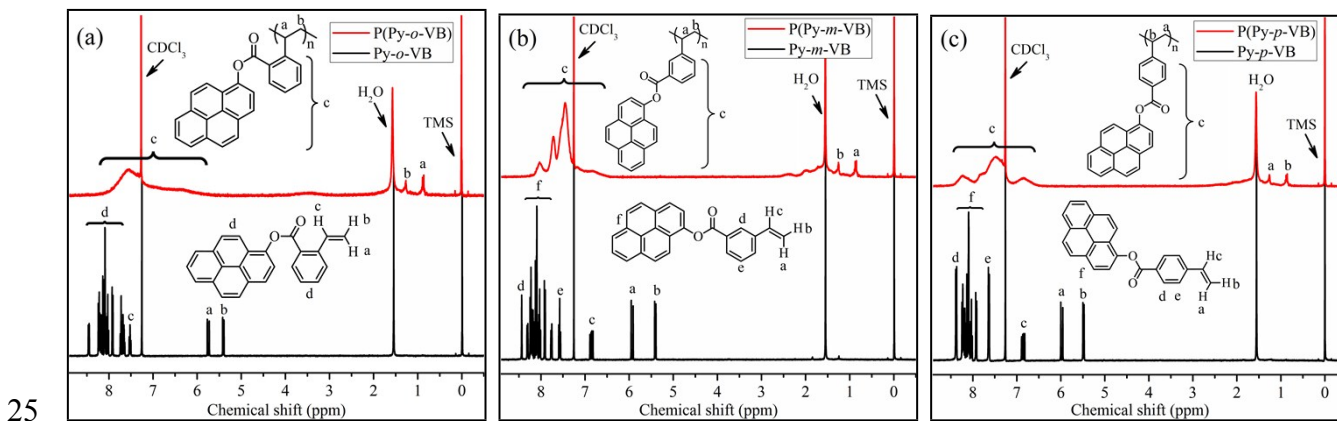


Fig. S1 ^1H NMR spectra of monomers Py-*o*(*m*, *p*)-VB and corresponding polymers P(Py-*o*(*m*, *p*)-VB) in CDCl_3

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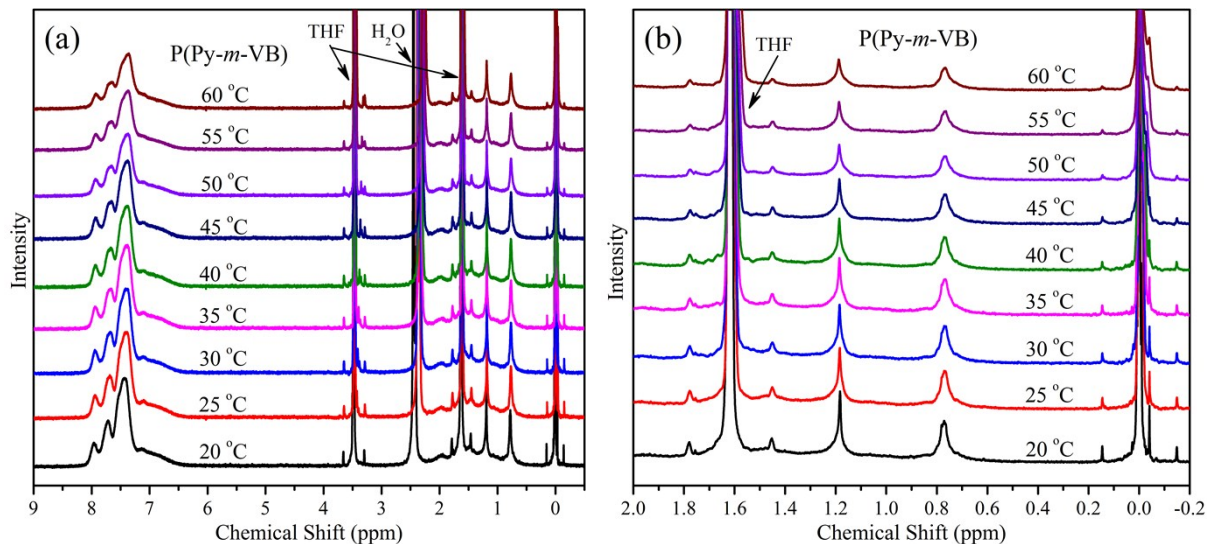
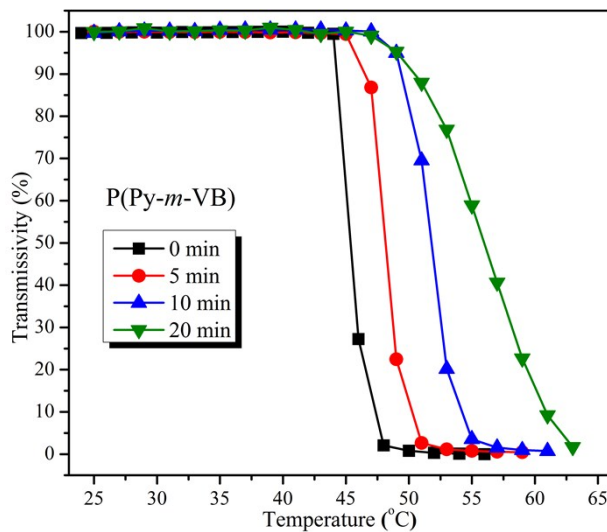


Fig. S2 ^1H NMR spectrum evolution of P(Py-*m*-VB) (a) and magnified ^1H NMR spectrum evolution of P(Py-*m*-VB) (b) in THF- d_8 on elevating the solution temperature.



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Fig. S3 Temperature dependence of transmittance at 800 nm for 5 mg/mL P(Py-*m*-VB) in THF during the heating processes before (square) and after photoirradiation for 5 (circle), 10 (up triangle) and 20 (down triangle) (cycle).

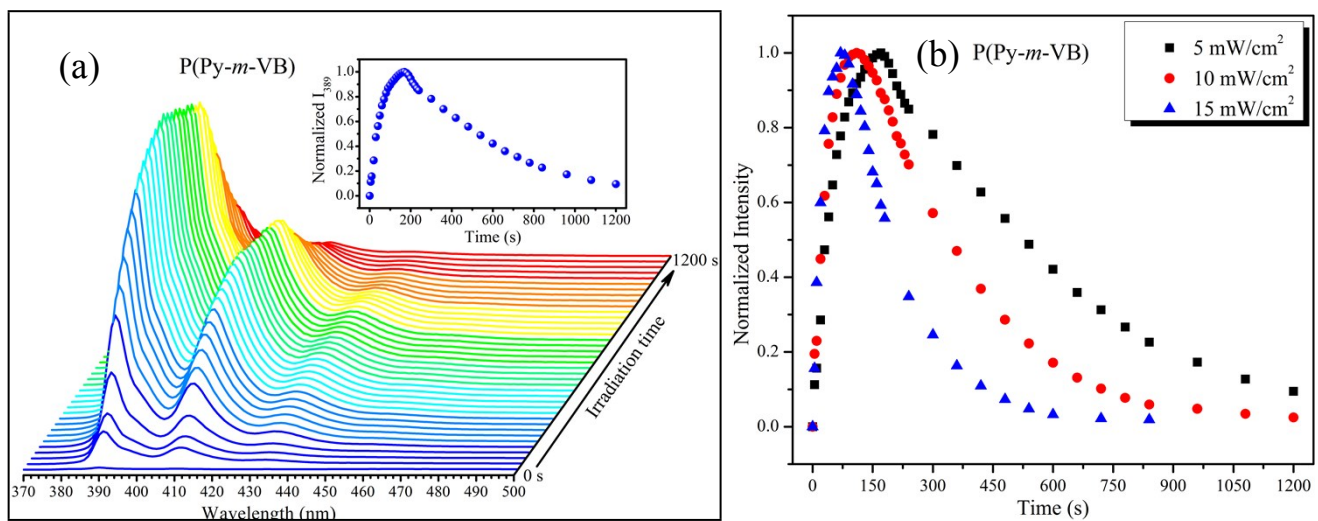


Fig. S4 (a) The fluorescence emission spectra of P(Py-*m*-VB) under UV irradiation (365 nm, 5 mW/cm²) of various period of time. (b) Luminescent intensity vs time for P(Py-*m*-VB) solution under UV irradiation of various intensities.

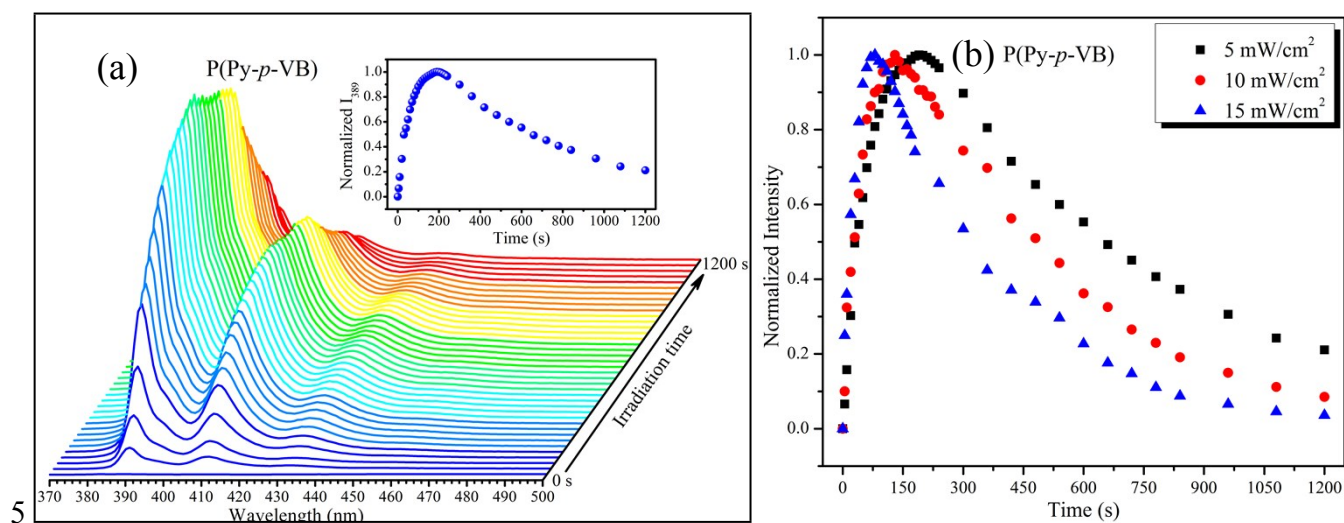


Fig. S5 (a) The fluorescence emission spectra of P(Py-*p*-VB) under UV irradiation (365 nm, 5 mW/cm²) of various period of time. (b) Luminescent intensity vs time for P(Py-*p*-VB) solution under UV irradiation of various intensities.