

## Supplementary Information

### Sol-gel transition of poly(3-hexylthiophene) revealed by capillary measurement: phase behaviors, gelation kinetics and formation mechanism

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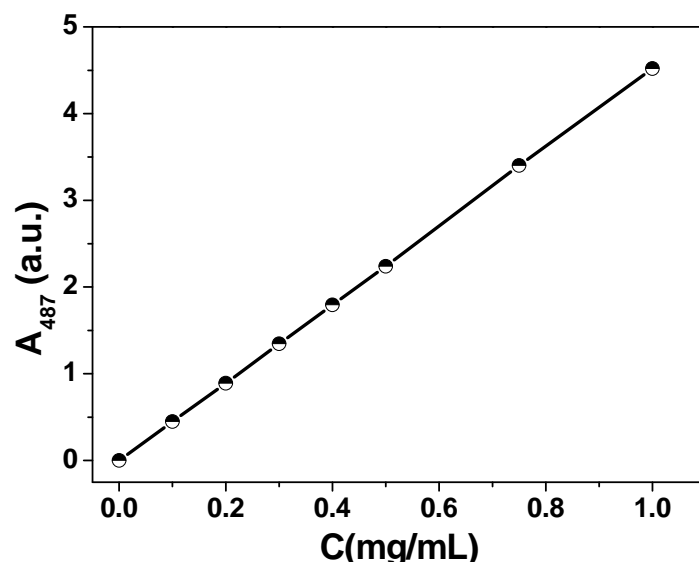


Fig. S1 Absorbance at 487 nm (isosbestic point) at a series of P3HT concentrations.

**Note:** P3HT dispersion has an isosbestic point at ~487 nm, which is independent of its aggregation state. Firstly, we measured the UV-Vis absorption spectra of P3HT solutions at a series of concentrations. The relationship between absorbance at 487 nm

(A<sub>487</sub>) with P3HT concentration was plotted as a working curve for determination of solubility. Afterwards, mixed solvents with different anisole contents ( $\phi$ ) were prepared. P3HT was added into 1 mL mixed solvents at a specific anisole volume fraction, and it was preserved at room temperature without heating or ultrasonic treatment, in order to obtain P3HT saturated solution. UV-Vis absorption spectra of these saturated solutions was measured, and their concentrations could be calculated by adopting the linear working curve.

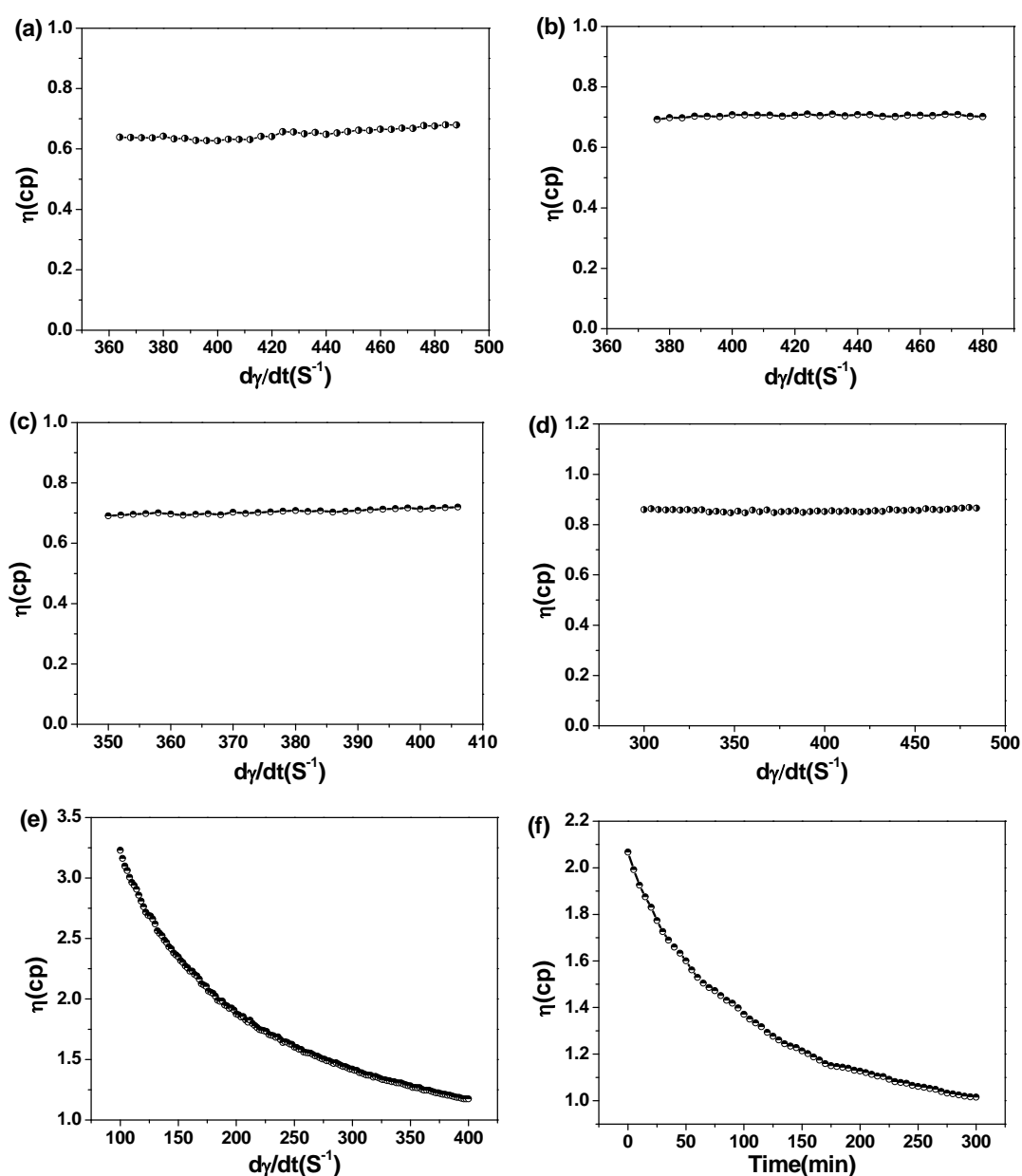


Fig. S2 Rheological properties of P3HT/chlorobenzene-anisole systems. Solution phase: (a)  $\phi = 0.75$ , 0.1 mg/mL; (b)  $\phi = 0.75$ , 0.2 mg/mL. Sol phase: (c)  $\phi = 0.75$ , 0.5 mg/mL; (d)  $\phi = 0.75$ , 1.0 mg/mL. Sol-gel blend: (e) and (f)  $\phi = 0.75$ , 1.5 mg/mL.

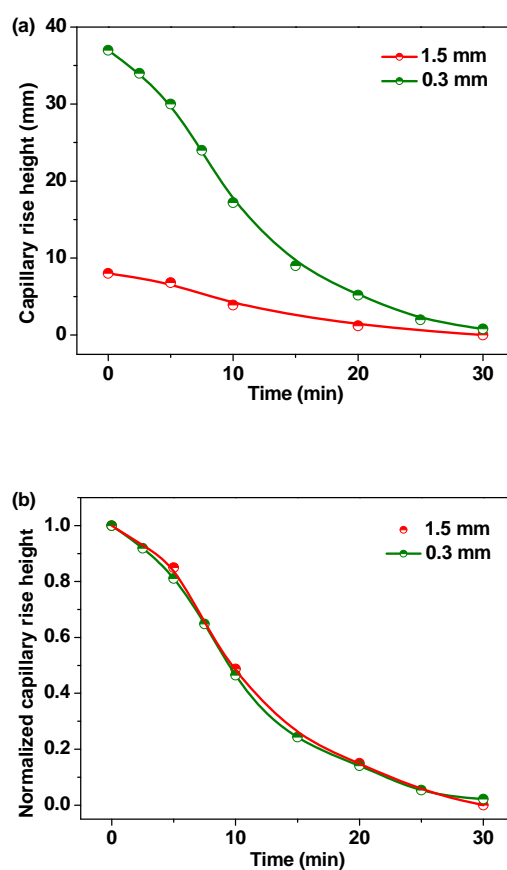


Fig. S3. (a) Capillary rise height curves versus time of P3HT/chlorobenzene-anisole ( $\phi = 0.8$ , 3 mg/mL) measured by capillary tubes with different inner diameters. (b) Normalized capillary rise height curves versus time.

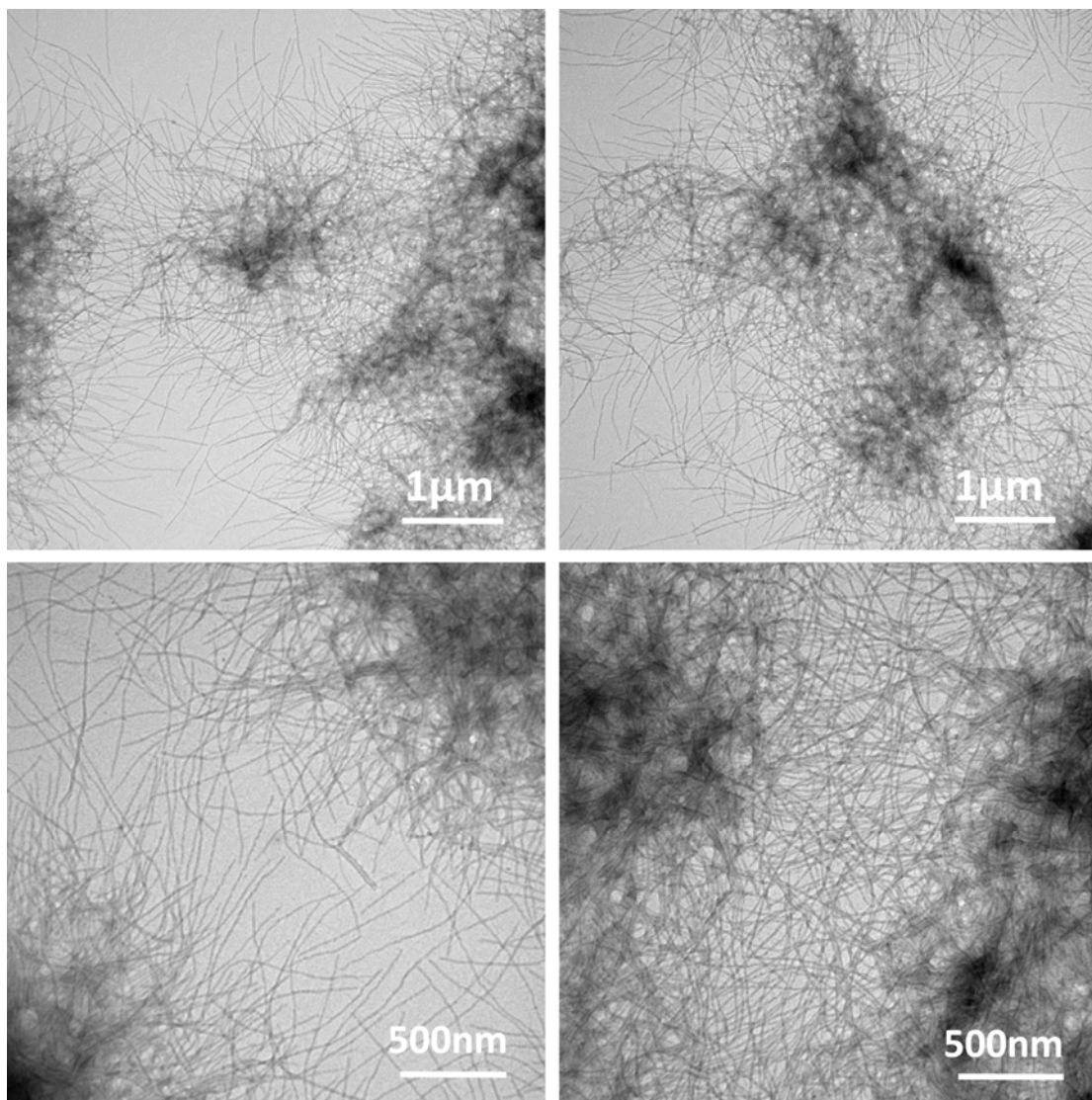


Fig. S4 TEM images of P3HT microgel clusters dropcast from P3HT sol preserved for 72 h ( $c = 1$  mg/mL,  $\phi = 0.75$ ).