

Preparation and Characterization of Polyfluorene-based Supramolecular π -Conjugated Polymer Gels

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Instruments and Methods

Pristine films of PFO were spin-casted on quartz substrates from its chloroform solution (8 mg/ml) using KW-4A (from the institute of micro-electronics of Chinese Academy of Science) at 3500 rpm for 30s. Pristine films was dipped in several pure solvent to obtain different contents of β -phase: 1,2-dichloroethane (DCE), dichloromethane (DCM), chloroform, chlorobenzene (CB), hexane and toluene. Another Pristine film was dipped in DCE with different dipping times to obtain the maximum content of β -phase without etching the film thickness which was monitor by UV-vise spectra. IR spectra

were recorded from 4000 to 800 cm^{-1} on a Shimadzu IR-Prestige-21 FT-IR spectrophotometer with a Mid-IR (MIR) globar source. The interferograms were recorded 32 times at the resolution of 4 cm^{-1} . A wideband mercury-cadmium-telluride (MCT) detector was used for the FT-IR measurement.

Results and Discussion

To gain insight into the solvent effect of self-assembly behavior in gelation, DCE was introduced in surface processing of spin-coating film as well as a series solvent. It is believed that a fraction of PFO molecular dissolve into solvent and self-assemble into “*beta*-sheet”, when the pristine PFO film swelled by solvent. Pristine films (spin-coated from chloroform) which considered as the amorphous were dipped in diversity solvent follow ref. 1. The thickness of film vs. times was monitor by absorption spectra in **Figure SI-1**. It implies that procedure with DCE dipping will form a considerable content of β -phase PFO nearly at the same proportion without etching the film in 2 min. But the thickness of PFO film will drop down when such procedure last 20 min. Theoretical β -phase absorption can be calculated by the subtraction of the absorption pristine film with that of DCE dip-processed film. Subtraction of the normalized curve yields the relative absorption by the β -phase component and thus the total percent β -phase in the film can be estimated by using the spectral deconvolution method.^{1, 2, 3} **Figure SI-2** shows the resulting β -phase absorption and its mirror image relationship with the photoluminescence (PL) spectra.

Figure SI-3 shows the change in the absorption and PL spectra of dip-processed film with variety solvent comparing to the pristine film. **Figure SI-3A** shows that there is a progressive decrease in the absorption maximum of the glassy PFO at 385 nm, with a concomitant increase of the β -phase absorption at 405nm and 435 nm. And the β -phase content of calculate result is setting out on **Table SI-1** together with the data take from the drop-casted film of different solvents. The DCE dip-processed film has got β -phase content of up to 30 %, which is highest of these solvent. The intensity of the peak at ~420 nm decreases with increasing β -phase content. The β -phase content has a rough analogical rule with the gelated formation where the moderately poor solvent is proved most effective. This result indicates that the solvent quality has a strong affect on the self-assembly behavior and α - to

β -conformational change from dipping processing. It also answers for the reference with the conclusion that the formation of the two phases during spin-coating is controlled reliably through the choice of the boiling point and solubility parameter of the solvent.^{4, 5} With this simple physical method Bazan *et al.* obtained 45% content of β -phase in film which is the largest content reported as we know hitherto.² Due to the scattering of PFO-CPOG and the absorption of DCE, the deconvolution method is inapplicable for gel system. However we still confirm the β -phase content in PFO-CPOG should be larger than 50% estimate roughly (see **Figure SI-4**).

References

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Supplementary Table

Table SI-1. Gelation experimental results of PFO and the β -phase contents in various solvents with different boiling points and solubility parameters.

| Solvent and gel | | DCE | Toluene | Hexane | CB | DCM | Chloroform |
|---|--------------------|------|---------|-----------------|------|------|------------|
| Boiling point (°C) | | 84 | 110 | 69 | 130 | 40 | 61 |
| Solubility parameter (cal/cm ³) ^{1/2} | | 9.8 | 8.9 | 7.3 | 9.5 | 9.7 | 9.3 |
| Gelation ^{a)} | | Y | N | N | N | P | N |
| β -phase fraction (%) ^{b)} | Dip-processed film | 30 | 18.8 | 18 | 10 | 7.4 | 4.5 |
| | Drop-cast film | > 50 | 18.4 | \ ^{c)} | 9.23 | 23.4 | 10.5 |

^{a)} Y = gelation, N = solution, P = precipitate. ^{b)} Dip-process films were spin-coated from chloroform, followed by dipping in various listed solvents; Drop-cast films were obtained by directly drop-casting from its solution. β -phase fraction was calculated by UV-vis absorption spectrum. ^{c)} PFO hardly dissolved in hexane even heating the solution, thereby no PFO film was obtained by drop-casted.

Supplementary Figures

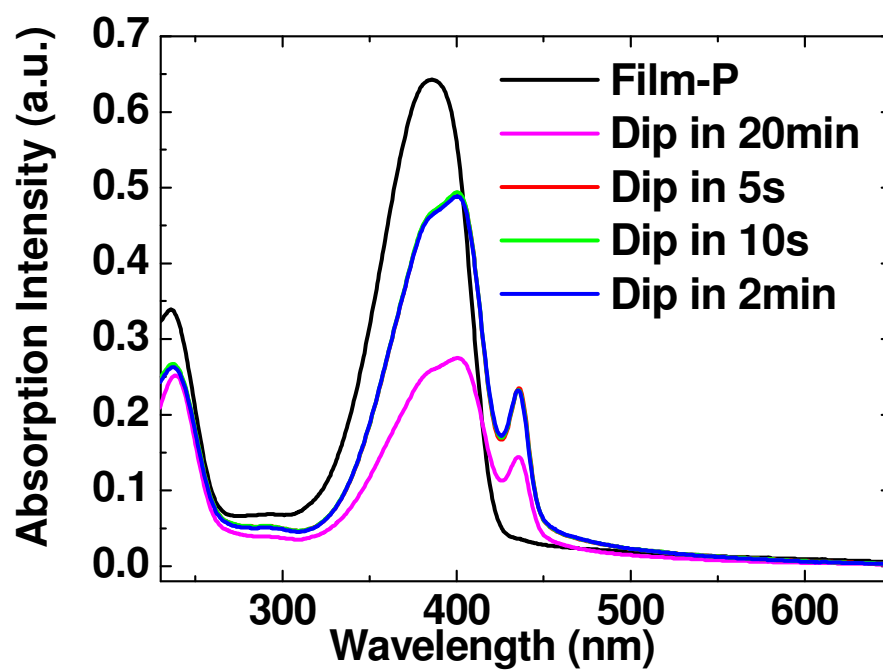


Figure SI-1. The UV-vis absorption spectra of the pristine films dipped into DCE for 5 s (red), 10 s (green), 2 min (blue) and 20 min (pink).

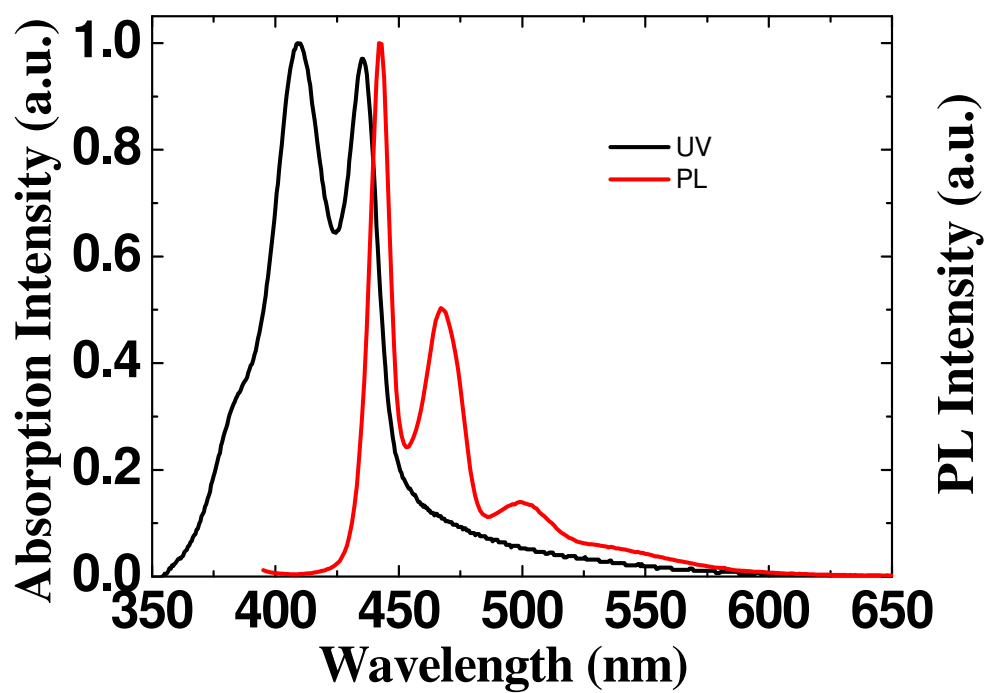


Figure SI-2. Calculated β -phase absorption and actual PL spectra of DCE dip-processed film.

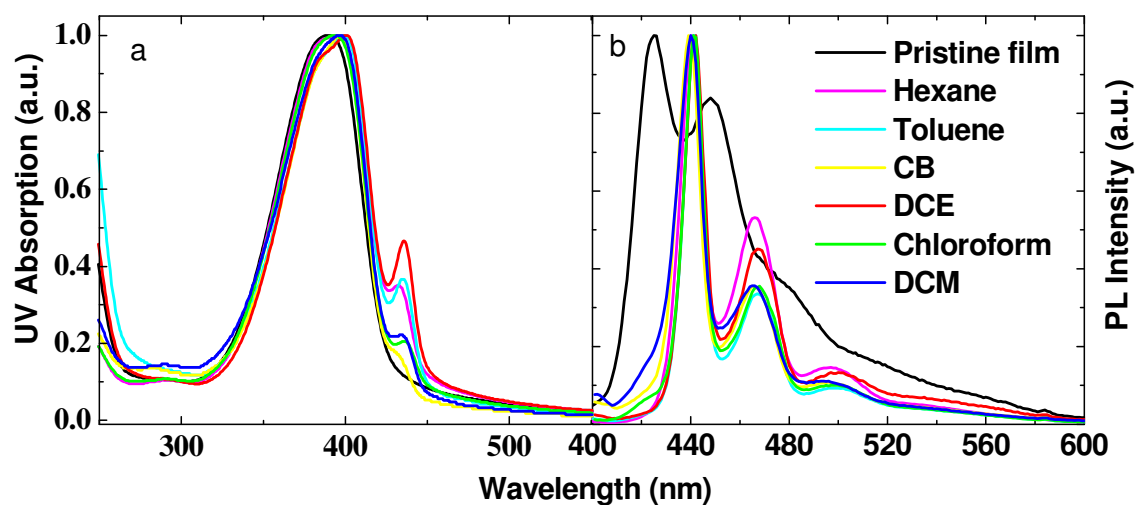


Figure SI-3. (a) Normalized absorption and (b) PL spectra of pristine PFO films dipped in a series of solvent: hexane, toluene, CB, DCE, chloroform and DCM.

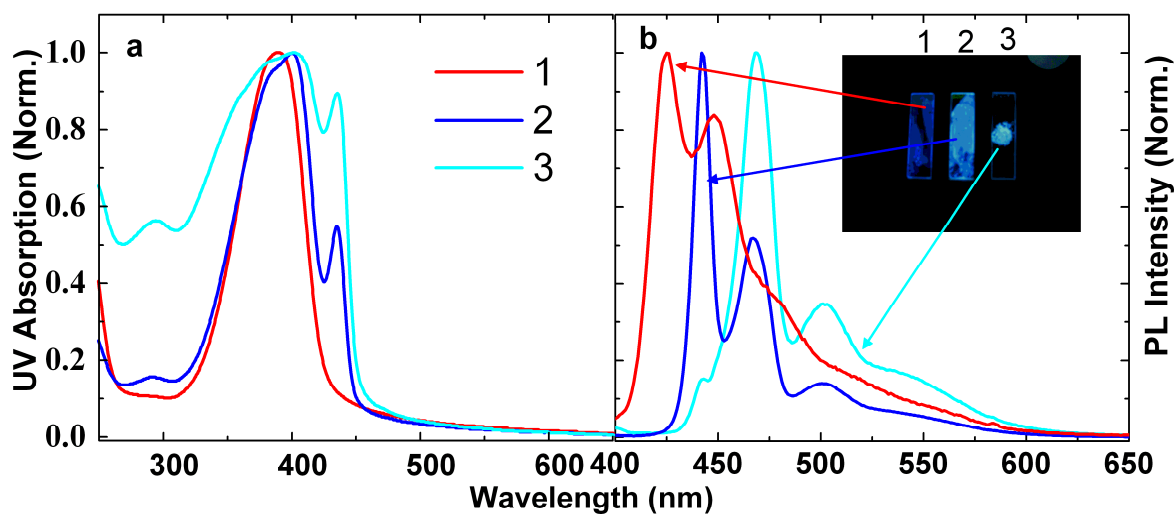


Figure SI-4. UV-*vis* absorption and PL spectra of PFO films. 1 is pristine film spin-coated from chloroform; 2 is PFO sol spin-coated film before it cool down; 3 shows the PFO/DCE gel sandwiched between two quartz glasses in order to obtain a $\sim 100\ \mu\text{m}$ thick gel film, record as the green line.

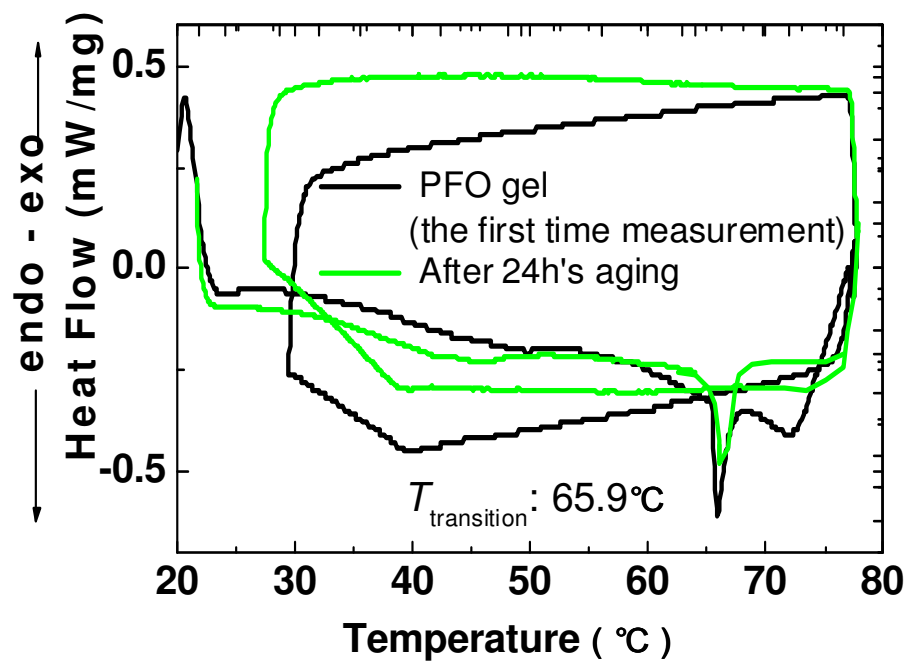


Figure SI-5. The whole cooling-heating cycles for DSC measurement of PFO/DCE gel from 30 to 80°C, together with the data obtained after aging for 24 hours.

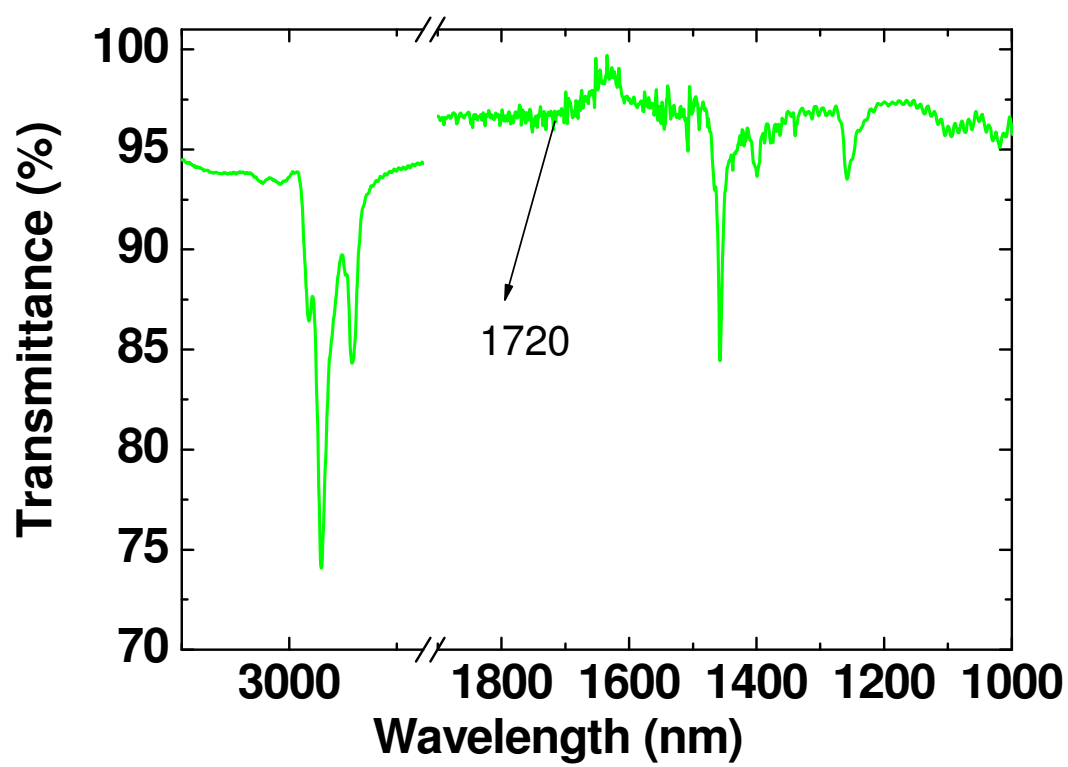


Figure SI-6. The FT-IR spectra of PFO used for the PFO/DCE gel preparation.

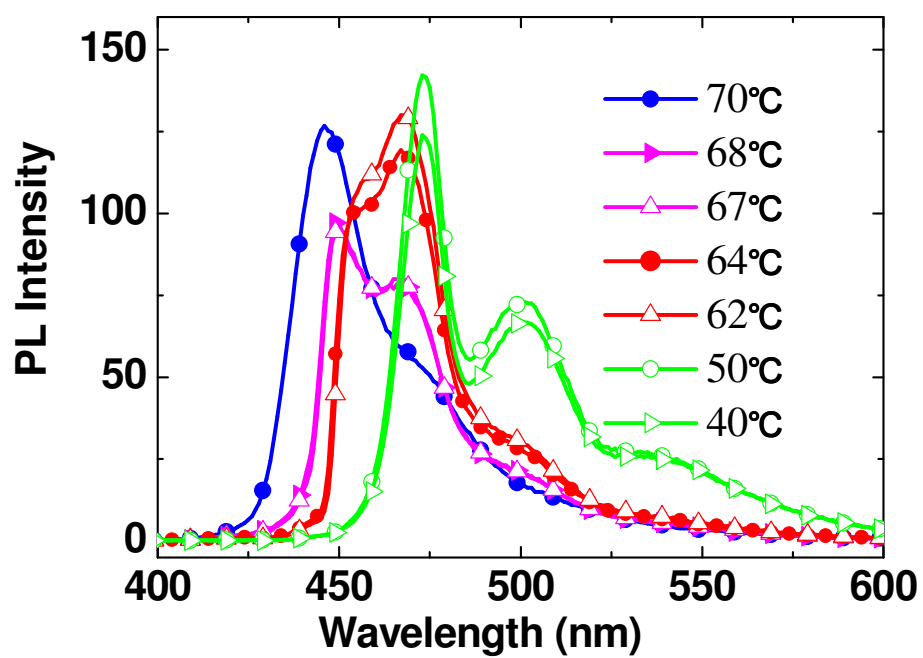


Figure SI-7. The PL spectras of PFO/DCE gel in 70, 68, 67, 64, 62, 50 and 40 °C.

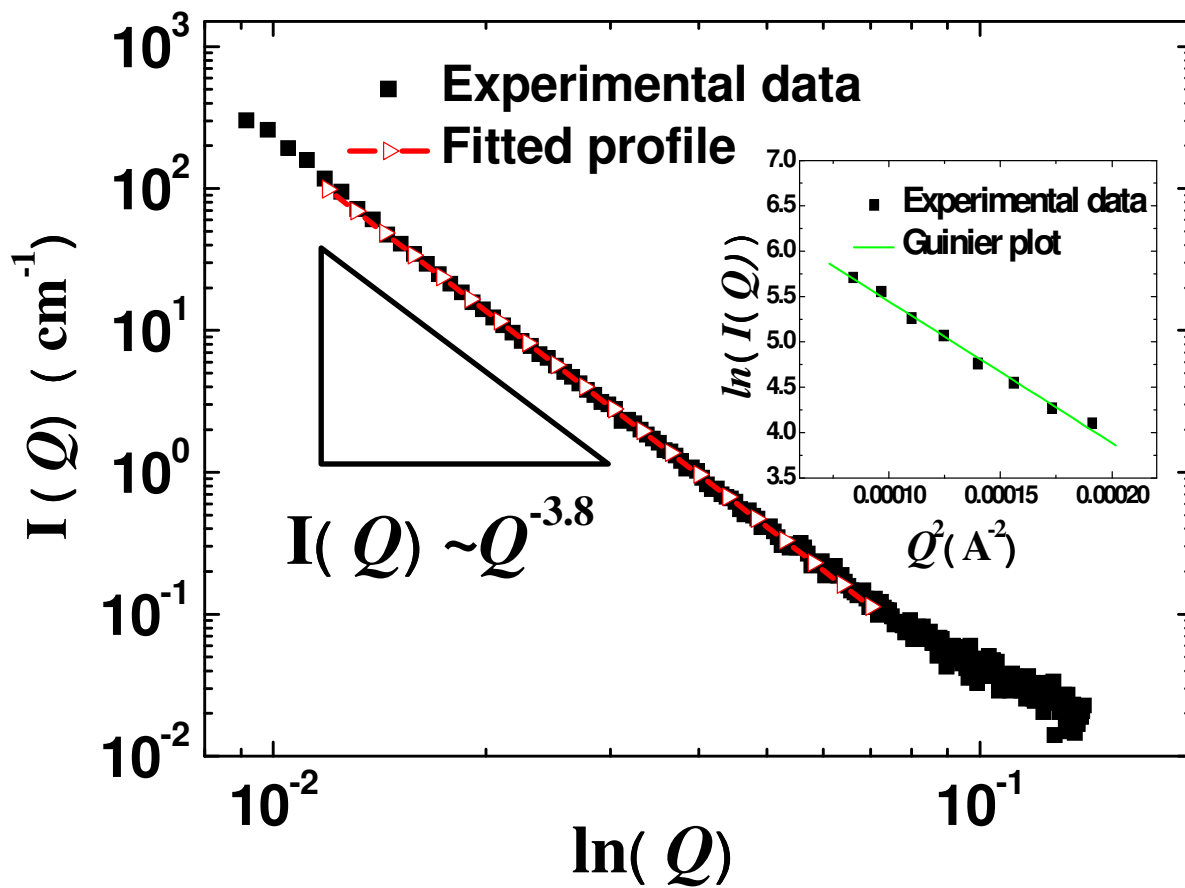


Figure SI-8. Scattering intensity of xerogel obtained at room temperature, $Q^{-3.8}$ power law for the sample signified the formation of irregularly sphericity scattering unit. The inset shows model-independent Guinier plots.