Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

A π-Conjugated Polymer Gelator from Polyfluorene-based Poly(tertiary alcohol) via Hydrogen-Bonded Supramolecular Functionalization

EXPERIMENTAL SECTION

Chemicals and Materials. 2,7-dibromo-9-(4-(octyloxy)phenyl)-fluoren-9-ol has been synthesized according to our previous literatures. Poly(9-(4-(octyloxy)phenyl)-2,7-fluoren-9-ol) (PPFOH) and Poly(9-(octyloxy) -9-(4-(octyloxy)phenyl)-2,7-fluorene) (PPFO8) have been synthesized via the typical Yamamoto polycondensation according to previous report.[4] The number-average molecular weights (M_n) and polydispersity index (PDI) of the PPFOH (Low M_n: PPFOH-L, High M_n: PPFOH-H) and PPFO8 are determined by GPC analysis with a polystyrene standard calibration (Figure S1). PPFOH-L and PPFOH-H have M_n of 1.04×10^4 with the PDI of 1.60, M_n of 2.47×10^4 with the PDI of 1.93, respectively, and PPFO8 with the M_n of 6.92×10^4 and PDI of 1.62. It is deduced that the degree of polymerization (DP) are estimated to be *c. a.* 29 for PPFOH, *c. a.* 70 for PPFOH-H and *c. a.* 140 for PPFO8. And the length of the repeat unit of the polymer chain, which includes an additional fluorene-to-fluorene, carbon-carbon single bond length, was calculated to be lr = 0.836 nm.[5] Therefore, the length of individual PPFOH-L, PPFOH-H and PPFO8 chains were about 24.2, 58.1 and 91.1 nm, respectively.

Characterizations: Gel permeation chromatography (GPC) analysis was performed on a HP1100 HPLC system equipped with 7911GP-502 and GP NXC columns using polystyrenes as the standard and tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min. Absorption spectra were measured with a Shimadzu UV-3600 spectrometer at 25 °C, and emission spectra were recorded on a Shimadzu RF-5301(PC)S luminescence spectrometer. The solution state spectra were measured in toluene solution. The film was prepared by spin-coating from toluene solution. The quartz cells of 10 mm thickness were used to measure the spectra. The samples were sandwiched between two quartz glasses to obtain gel layers of about 100 μm in thickness. PL spectra measurement of PPFOH solution (> 0.01 mg/ml) by using the front-face detections from a 1.0 cm cuvette according to previous report.[6] The differential scanning calorimetry (DSC) analyses were performed on a Shimadzu DSC-60A Instrument 0 at a heating rate of 5 °C/min. Dynamic light scattering (DLS, ZetasizerNano-ZS) measurements were carried out at a wavelength of 633 nm using laser as the light source at room temperature. The time-dependent autocorrelation function of the scattered light intensity was measured at an angle of 90°. The DLS measurements were usually repeated at least three times, and the average values were reported. The equipment and experimental parameter of fluorescence lifetime measurements: the incident 390 nm, 150-fs laser pulses were generated from a Coherent TOPAS-C optical parametric amplifier; pumped by a 1 kHz Coherent Legend regenerative amplifier that is seeded by a Coherent Vitesse oscillator. These input laser pulses were focused by a lens (f = 20 cm) on the samples solution in a 1-mm-thick quartz cell (beam spot ~1 mm inside the cell). The emission from the samples was collected at a backscattering angle of 150° by a pair of lenses and directed to an Optronis Optoscope^{TM} streak camera system which has an ultimate temporal resolution of 6 ps.

Preparations of PPFOH solutions and gels. The preparation of PPFOH solutions were carried out by dissolving polymer in the organic solvents spontaneously overnight. Various solvents in analyzing the case of PPFOH gelator were prepared by agitating their solution at *ca.* 80 ˚C for 10 min, where a macroscopically homogeneous solution was observed by the naked eye. The PPFOH-based gel was prepared by aging the solutions with the different concentrations at room temperature (25 °C). The methods of analyzing the critical concentration of formation gel in various solvents were as follows: a weighted amount of the PPFOH-L was 16 mg. And solvents of 0.05 ml were added into a sealed glass vial successively.

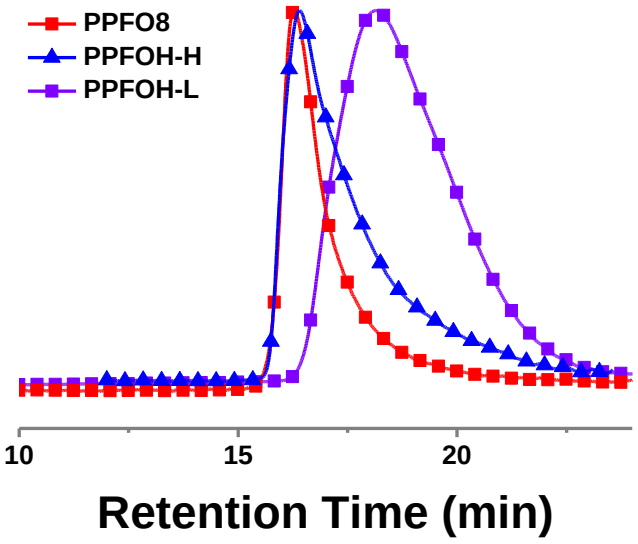


Figure S1. GPC analysis of PPFOH and PPFO8.

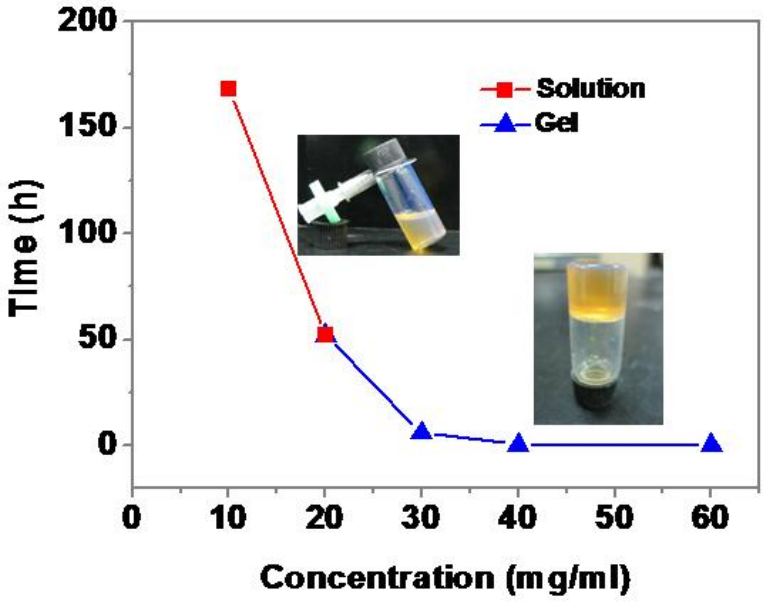


Figure S2. The gel formation of PPFOH-L in toluene at various concentration with different aging time.

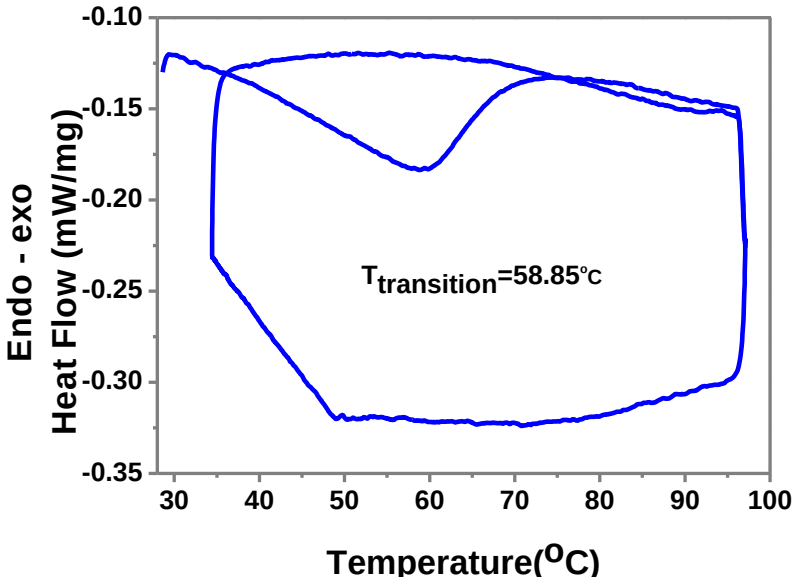


Figure S3. Cooling-heating cycles for DSC measurement of PPFOH-L/toluene gel from 30 to 100 ˚C .

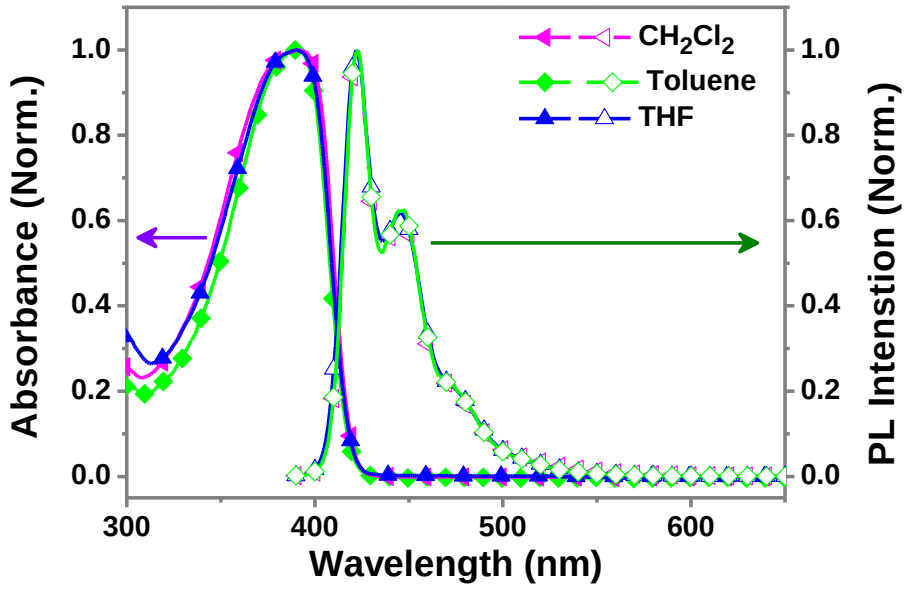


Figure S4. Absorbance and PL spectra of PPFO8 in various solution (concentration: 0.01 mg/ml). (Excited at 390 nm)

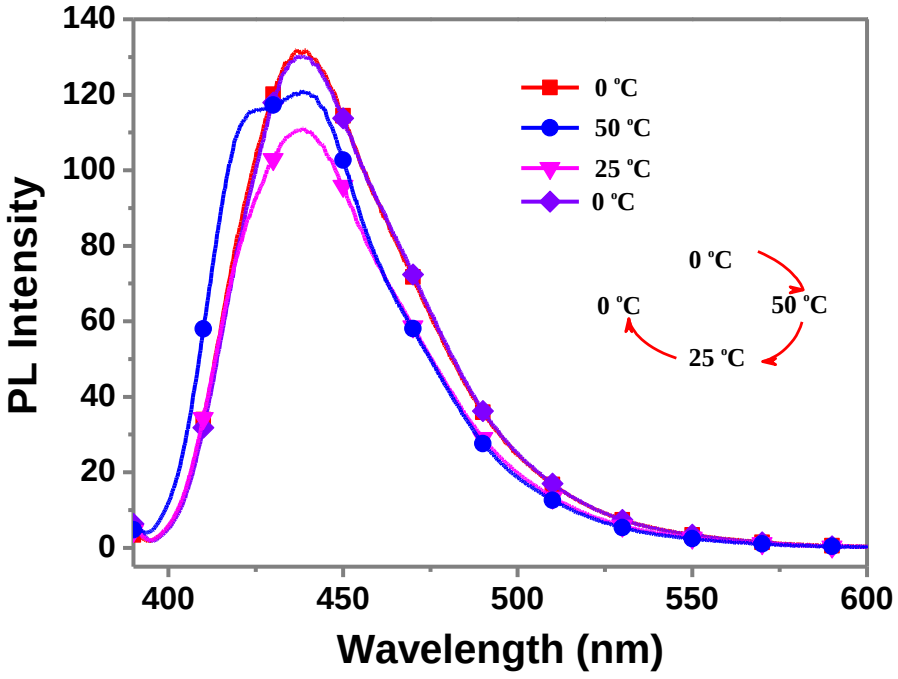


Figure S5. Emission spectra of PPFOH-L in toluene at 0, 25 and 50 °C. (Excited at 390 nm)

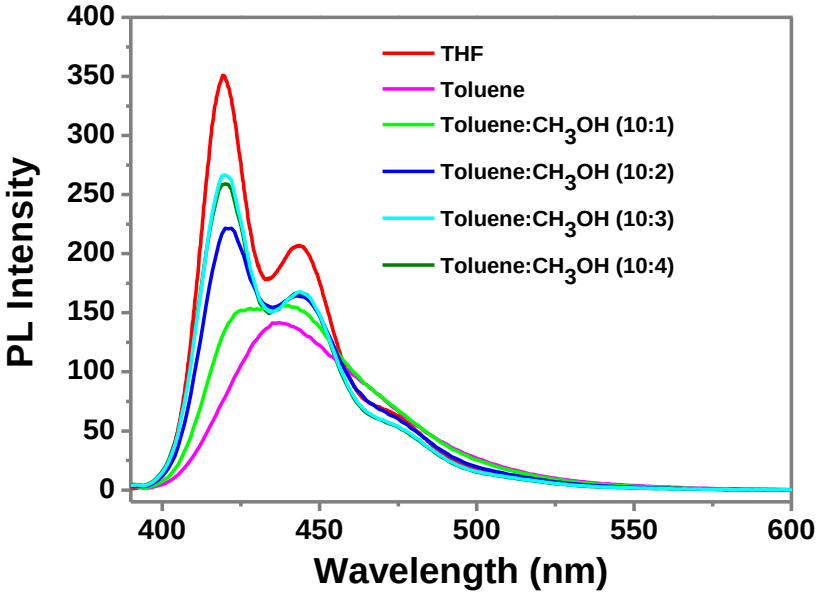


Figure S6. Emission spectra of PPFOH-L toluene solution with the addition amount of methanol. (Excited at 390 nm).

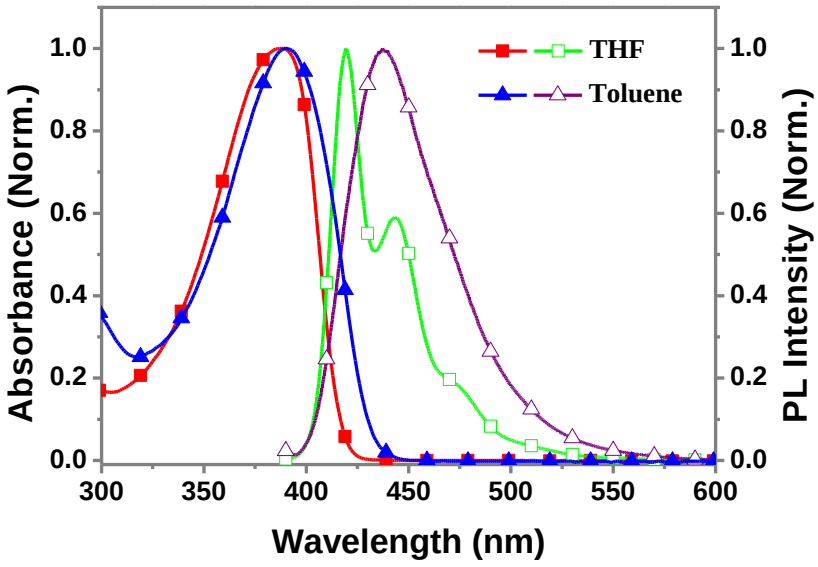


Figure S7. The UV-*vis* and PL spectra of PPFOH-L in THF and toluene. (Excited at 390 nm)

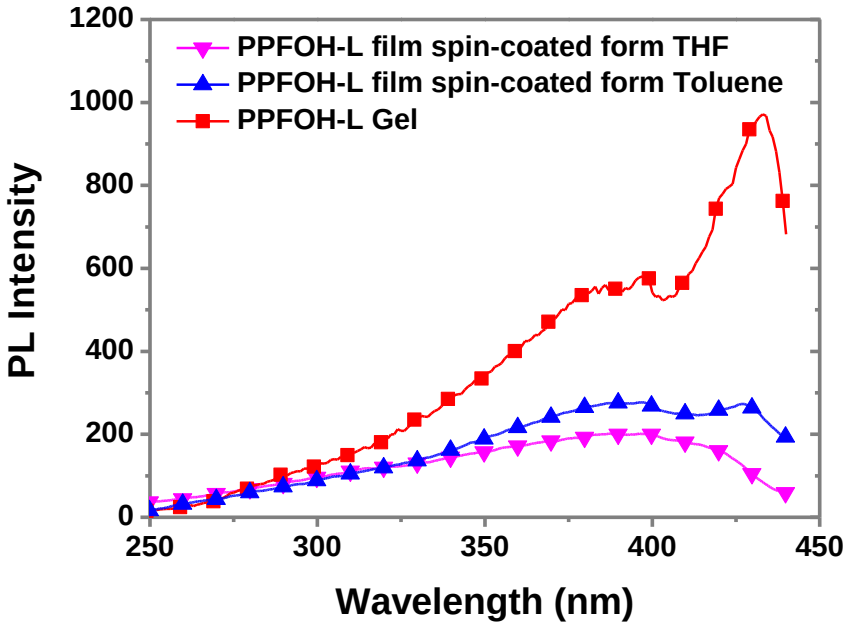
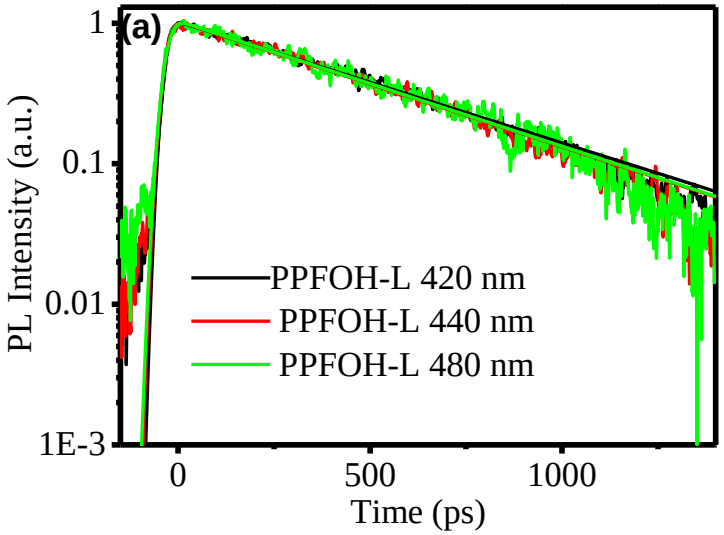


Figure S8. PLE spectra of PPFOH-L/toluene gel and films spin-coated from THF and toluene solution. (Emission at 460 nm)



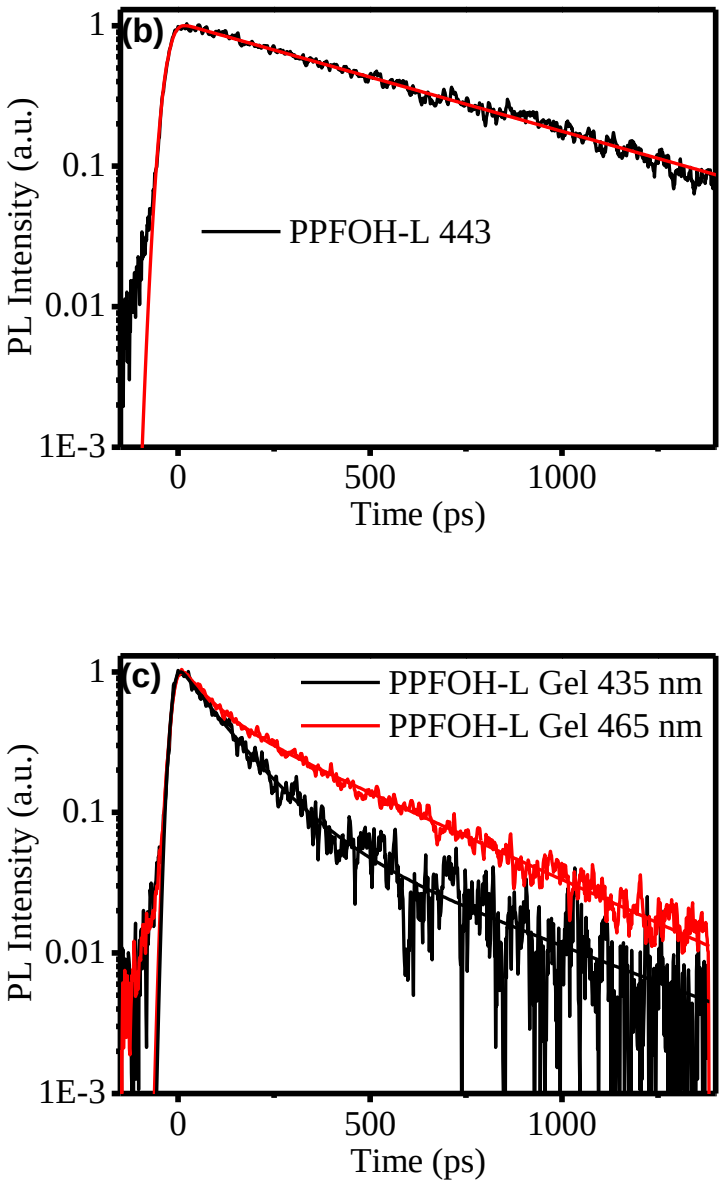


Figure S9. PL decays of PPFOH-L in solution and gel. (a) PPFOH-L in THF solution. (b) PPFOH-L in toluene solution. (c) PPFOH-L/toluene gel.

Table S1. Gelation behavior of PPFOH in various solvents at 25 °C [a]

Solvent	hexane	toluene	1,4-dioxane	DCE	cyclohexanone
	I	G (20 mg/ml, 52 h)	S	G (40 mg/ml, 1 h)	I
Solvent	THF	chloroform	ethanol	1,2-dichlorobenze	bromobenzene
	S	G (80 mg/ml, 18 h)	I	G (60 mg/ml, 10 h)	G (38 mg/ml, 10 h)
Solvent	DMF	DCM	acetone	methanol	acetonitrile
	S	G (70 mg/m, 26 h)	S	I	S
Solvent	aether	carbon tetrachloride	ethyl acetate	chlorobenzene	benzene
	S	G (20 mg/ml, 48 h)	S	G (26 mg/ml, 18 h)	G (40 mg/ml, 18 h)

[a] S: soluble. G: gel. I: insoluble. In prenthesis: critical gel concentration (CGC) (mg/ml) is the minimum concentration required for the formation of a stable gel at 25 °C, aging time (h).

Table S2. Gelation behavior of PPFOH in toluene at different concentrations.

Concentration (mg/mL)	60	45	30	20	10	7
Gelation	Y	Y	Y	Y	N (P)	N (T)
Time	0.2 h	0.5 h	6 h	52 h	168 h	-

[a] Y: Gel; N: no gel; P: precipitation (partial gel); T: transparent solution

Table S3. Gelation experimental results of PPFOH in various solvents with different boiling points, polarity points and solubility parameters.

Solvent and gel	PPFOH	PPFO8	Toluene	DCE	THF	DMF	n-hexane
Boiling point (˚C)	-	-	110	84	65	153	69
Polarity	> 0	0	2.4	3.0	4.2	6.4	0
Solubility parameter $(cal/cm^3)^{1/2}$	-	9.3	8.9	9.8	9.9	12.1	7.3
Gelation[b]	-	-	Y	Y	N	N	P

[a] concentration: 30 mg/ml, aged time: 8 h. [b] Y: gel; N: solution; P: precipitation.

Table S4. Summary of decay time of PPFOH-L solution and gel (toluene) at different PL wavelength.

Sample	λ nm	A_1	τ_1 (ps)	A_2	τ_2 (ps)
PPFOH-toluene	443	1	563		
	420	1	503		
PPFOH-THF	440	1	486		
	480	1	486		
PPFOH-Gel	435	0.10	424	0.90	112
	465	0.46	351	0.54	73

[a] The excitation wavelength was 390 nm, and the PL emission maxima were monitored in each case. The concentration of PPFOH toluene solutions was 10^{-2} mg/ml.

Reference

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