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Supporting Information

Aggregation-Induced Emission Lights Up the Swelling Process: A New Technique for Swelling Characterisation of Hydrogels

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Experimental Section

Materials: PVA (Mowiol ® 28-99, CAS No: 9002-89-5, molecular weight 145,000 and degree of hydrolysis > 99%), acrylic acid monomer (AA), ammonium persulfate (APS) as an initiator and N, N′-Methylenebis (acrylamide) (MBA) as a crosslinking agent, 1, 1, 2, 2-Tetraphenylethylene (TPE, CAS No: 632.51.9), poly(acrylic acid), partially sodium salt-graft-poly(ethylene oxide) (CAS No: 432784) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich, Australia.

Sample preparation: A stock solution of TPE in THF with a concentration of 100 mM was prepared by dissolving 1.662 g of TPE in 50 mL THF. The solution was stored in a refrigerator at 4°C for further use. PVA solution (6% w/w) was prepared by mixing PVA powder in distilled water under constant stirring at 800 RPM at 70 °C for 4 h. PVA solutions were kept overnight at room temperature in sealed containers. PVA films and mats were prepared by solvent casting and electrospinning, respectively.

Synthesis of the PAA hydrogel followed previous work. Briefly, 3.7 g AAwas dispersed in 3.5 cm^3 distilled water at 5 °C. A 0.45 g cm^{-3} NaOH solution was prepared by dissolving 1.63 g sodium hydroxide powder in 3.62 g distilled water, followed by cooling in an ice-water bath for 10 min. NaOH solution was then added dropwise into the AA solution with magnetic stirring at 5 °C for 20 min. Finally, 0.025 and 0.25 g MBA and 0.08 g APS powder were added into the mixture following by vigorous shaking by an IKA Vortex 3 shaker to ensure homogeneity. The mixture was poured into a glass mold and placed in an oven at the preset temperature of 60 °C for 10 min. Heating continued for the next 20 min with the temperature increased from 60 to 80 °C at the rate of 1 °C min^{-1}. After the overall heating duration of 30 min, prepared hydrogels were cooled to room temperature for 2 h while remaining in the oven. The synthesized PAA samples were peeled from the mold and stored in sealed bags at 4 °C for testing. Partially sodium salt-graft-poly (ethylene oxide) was used as SAP without any purification.

Methodology: The swelling behavior of samples (PVA, PAA, and SAP) was tested gravimetrically by measuring the initial weight of the dry samples and subsequently after they were immersed into distilled water until equilibrium. For measurement of swelling properties using FL intensity, small amount of hydrogel were placed in a standard cuvette, then 3 mL of swelling environment (water + TPE/THF with different water fractions) was added and the FL intensity of the swelling environment was detected at different time points using a fluorescent spectrophotometer (Cary Eclipse, Agilent Technologies) at the excitation wavelength of 350 nm (λ_{ex}). The emission wavelength was 470 nm (λ_{em}). Special attention was paid to ensure that the initial weight, volume and thickness of the hydrogels was low enough to avoid over-swelling. The over-swelling results in uptake of the entire swelling media and significantly affect the results. For characterization of TPE at different water fractions, the same method was employed without using hydrogel samples. The concentration of TPE within the swelling media was varied for different water fractions with the highest concentration of 4 mM at 80% water fraction. For the water fractions greater than 97%, the concentration of TPE was less than 0.5 mM. The initial concentration of TPE for a known water fraction kept constant across all experiment. For DSC experiment (TA Instruments, USA), PVA hydrogels were weighed and placed in an aluminum pan and heated at a scanning rate of 5 °C/min from 40 to 250 °C. A nitrogen purge through the sample chamber was implemented to obtain a more uniform, stable thermal environment.

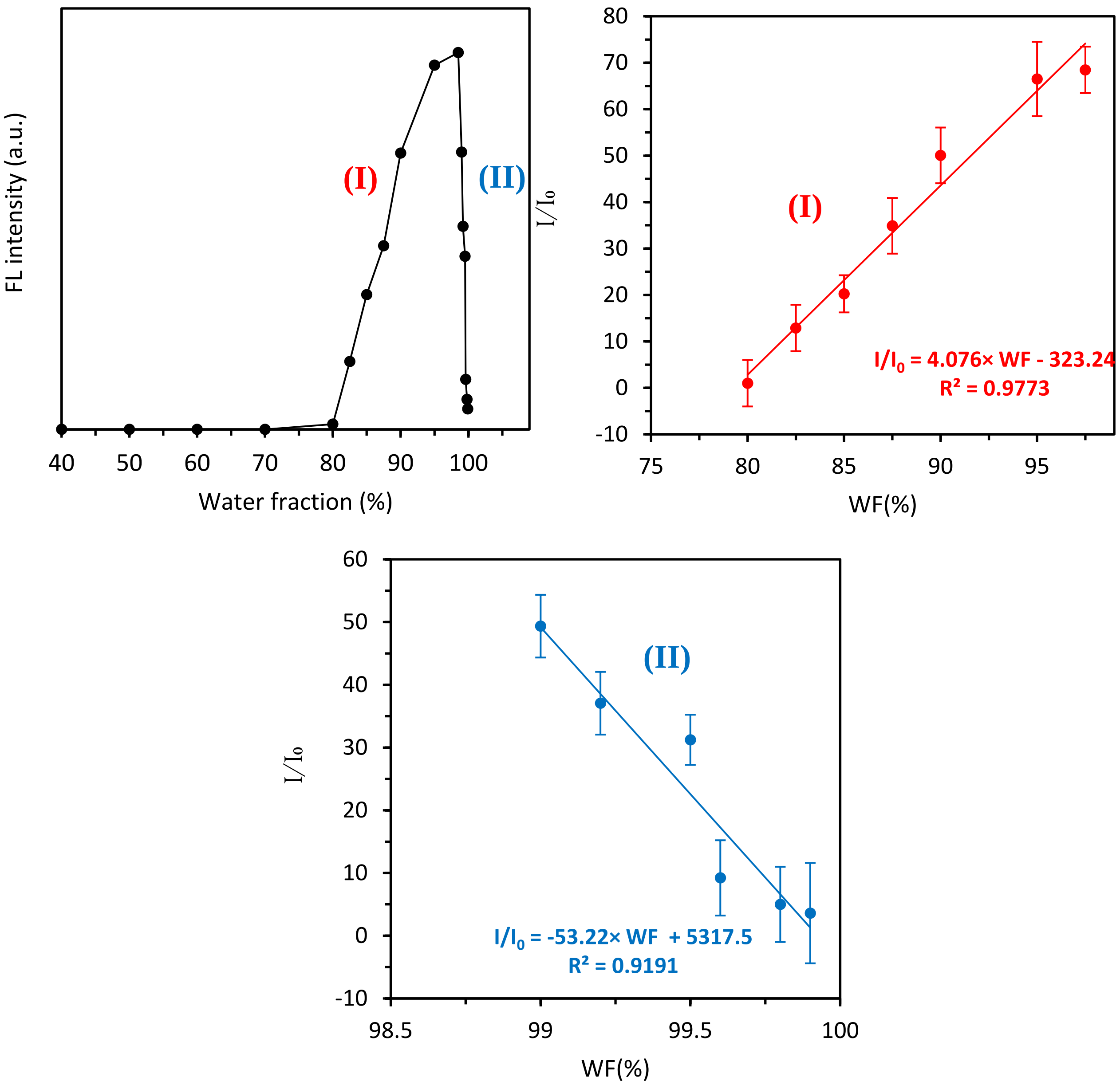

Figure S1. Changes in relative FL intensity for TPE at different water fractions (WFs). 20 mM solution of TPE in THF was added to different fractions of water-THF and the FL intensity was measured at different WFs from 0 to 99.9%. For WF less than 80%, the FL intensity was zero. An increase in relative FL intensity was observed for 80% < WF < 99.8%. Over the range of 99.8% to 99.9% the FL intensity decreased. For these two trends (labeled (I) and (II)), the relative FL intensity vs WF was identified using 3 measurements. Excitation and emission wavelengths were 350 and 470 nm, respectively.

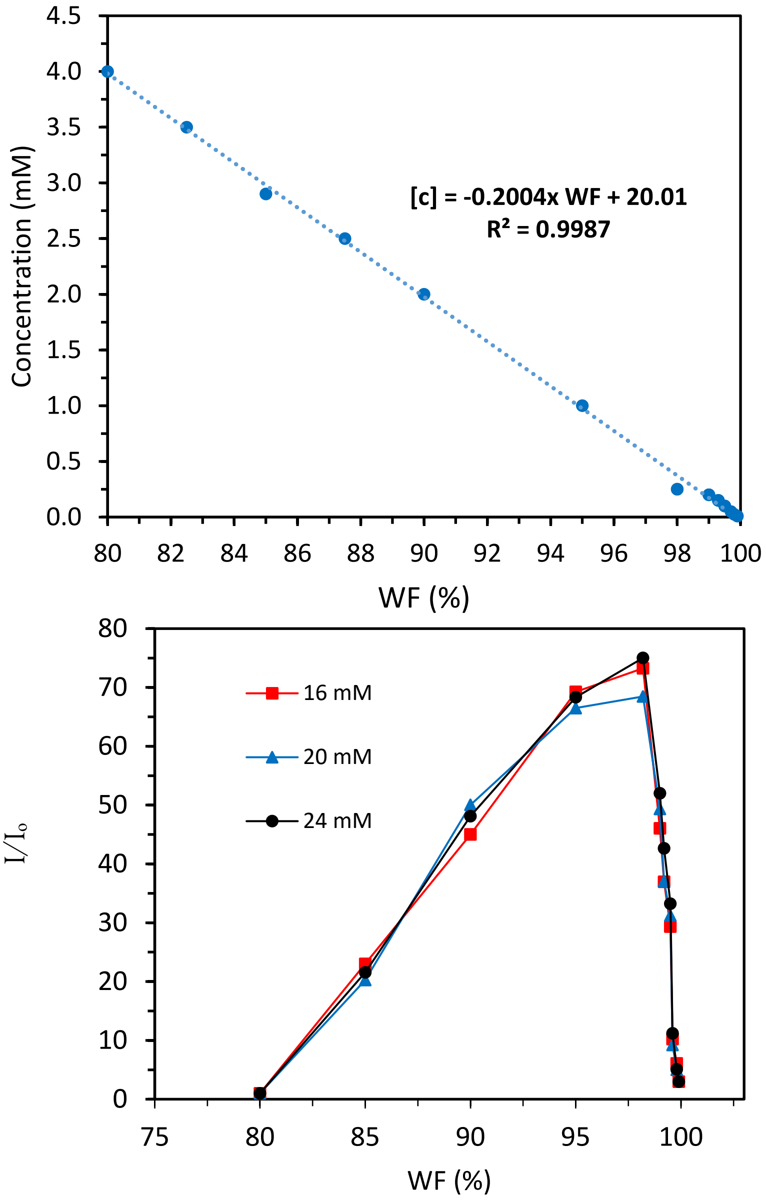

Figure S2. Change in concentration of TPE vs. WF and the effect of concentration on the relative FL intensity at different WFs. At different WFs, the final concentration of TPE was calculated (Table below) and the calibration curve for concentration vs. WF was prepared.

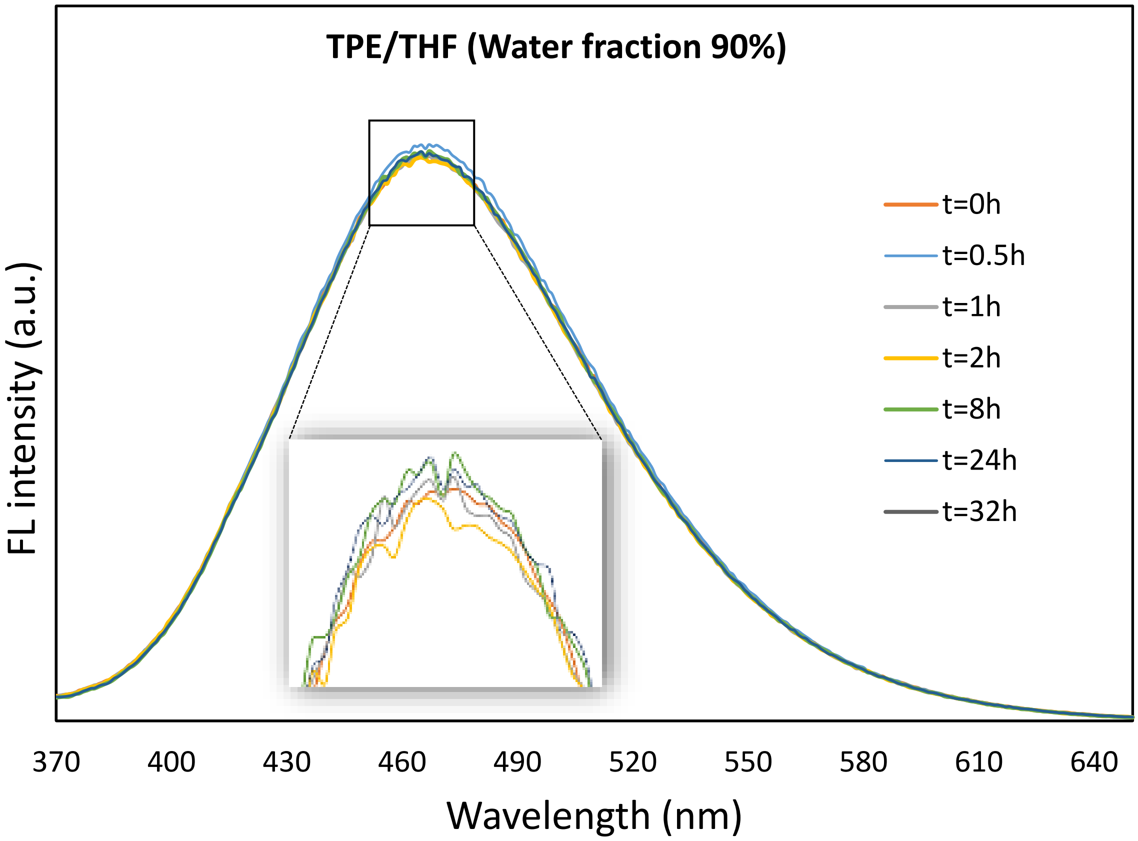

Figure S3. Stability of FL spectra for TPE/THF solution in water (WF=90%). 222 µL of TPE in THF (20 mM) was added to 2000 mL distilled water and the FL spectra were measured over time.

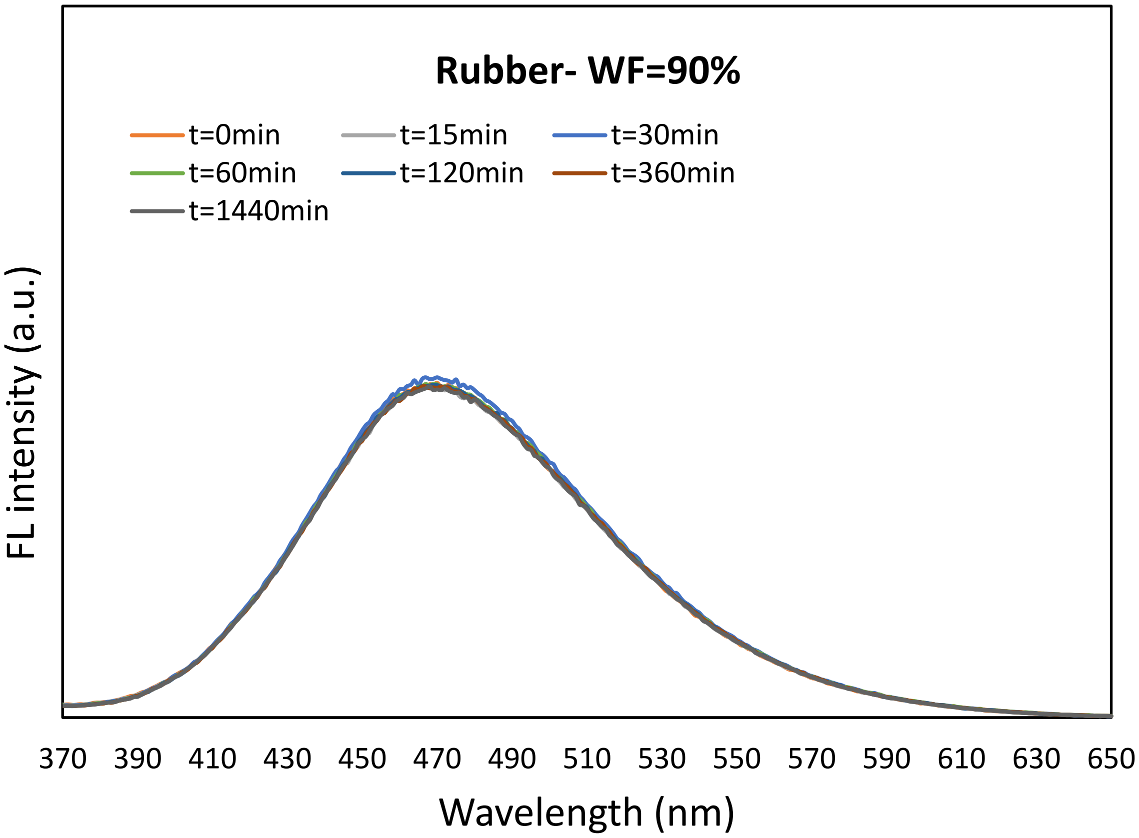

Figure S4. Change in FL spectra of swelling environment during the swelling of rubber (non-swellable polymer; control). The WF was 90% and the initial concentration of TPE/THF was 20 mM.

Table S5. DSC results for PVA film (6% w/w) at 1 and 4 FT cycles

Sample	F/T cycle	ΔH (J/gr)	% Crystallinity	Latent heat (mJ)
PVA film	1	55.2	39.5	78.2
	4	69.5	50.1	131.2

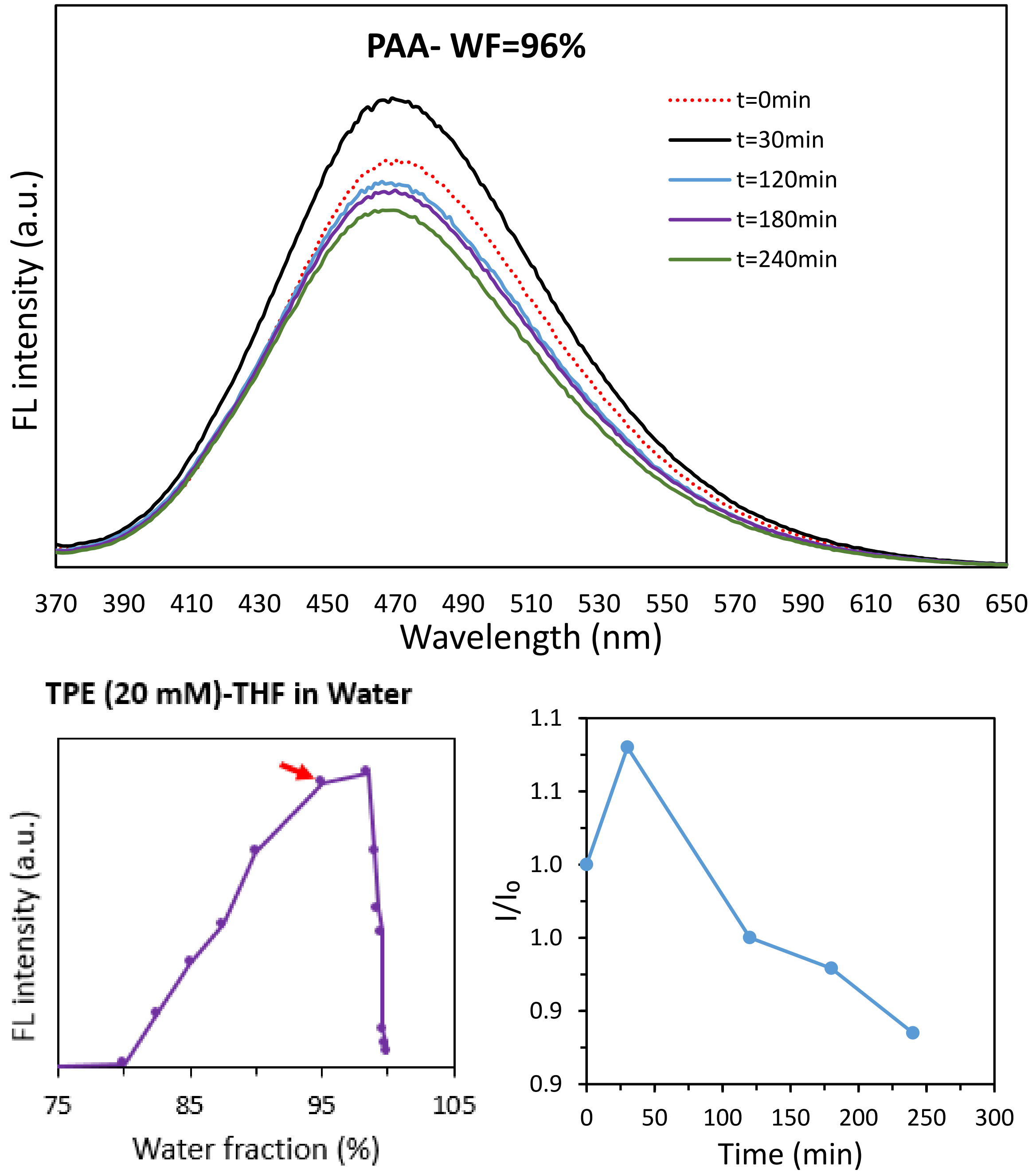

Figure S6. Change in FL spectra and relative FL intensity during the swelling process of PAA film at WF= 96%.

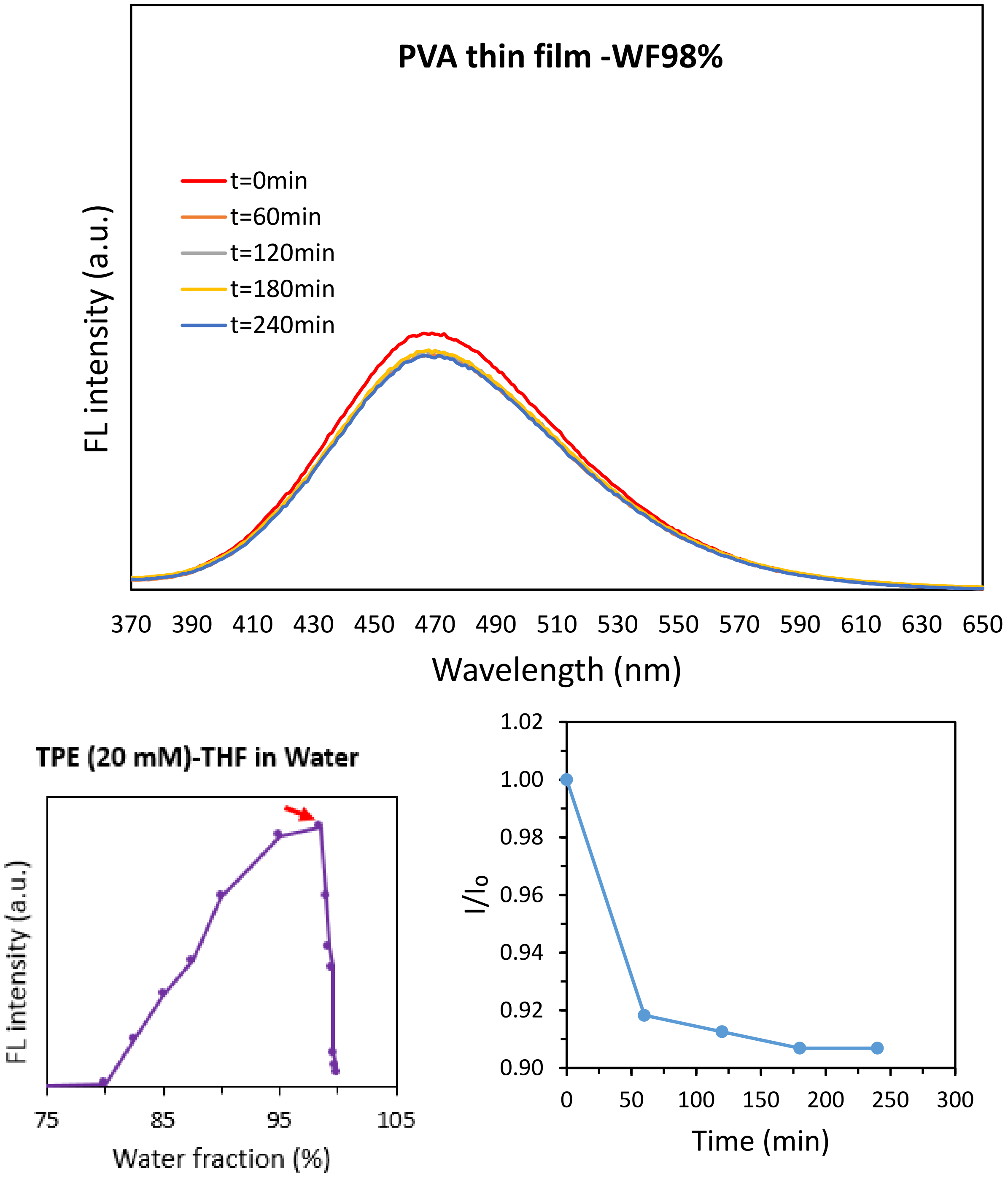

Figure S7. Change in FL spectra and relative FL intensity during the swelling process of PVA thin film at WF= 98%.

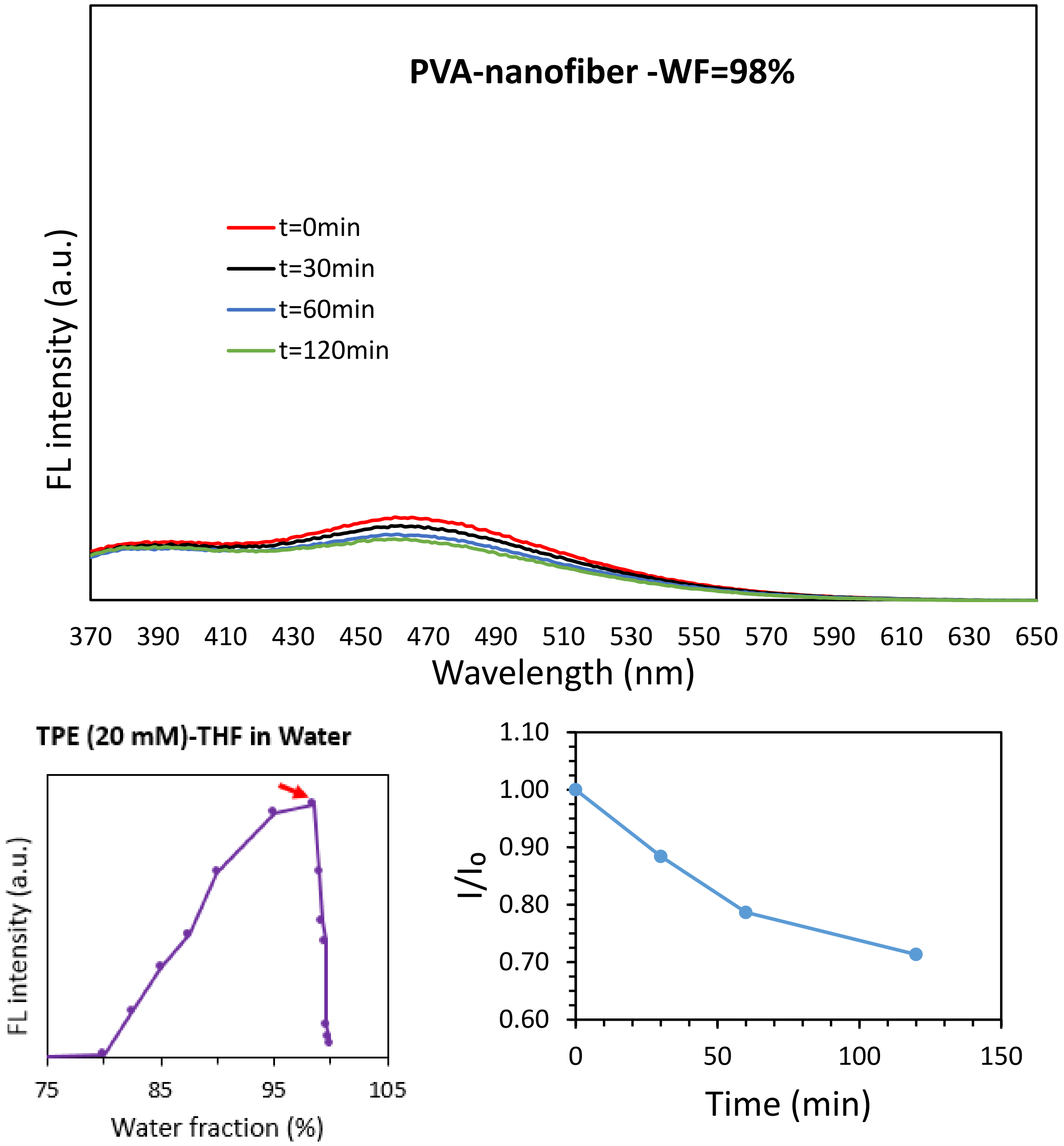

Figure S8. Change in FL spectra and relative FL intensity during the swelling process of PVA mat at WF= 98%.

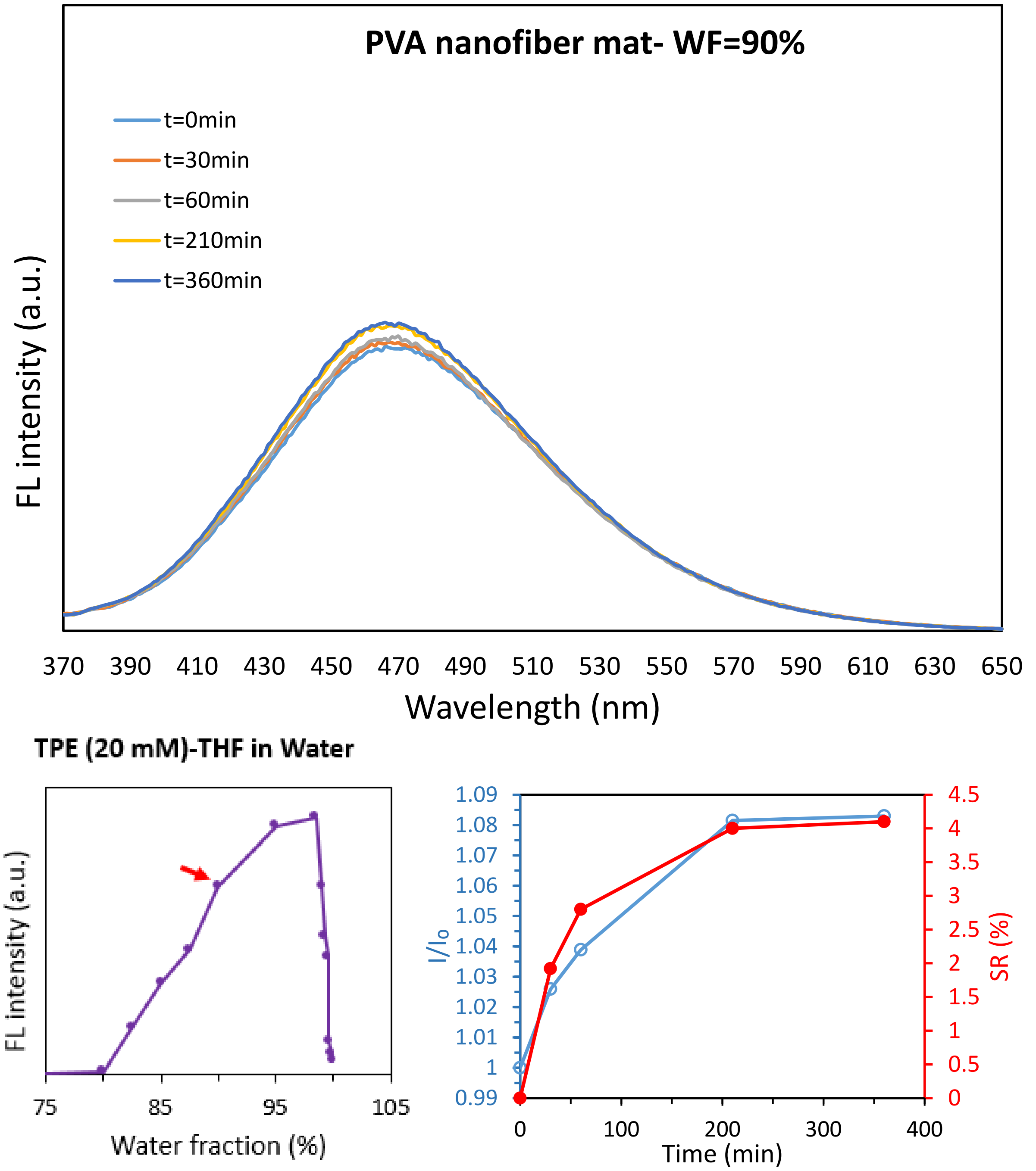

Figure S9. Change in FL spectra and relative FL intensity during the swelling process of PVA mat at WF= 90%.

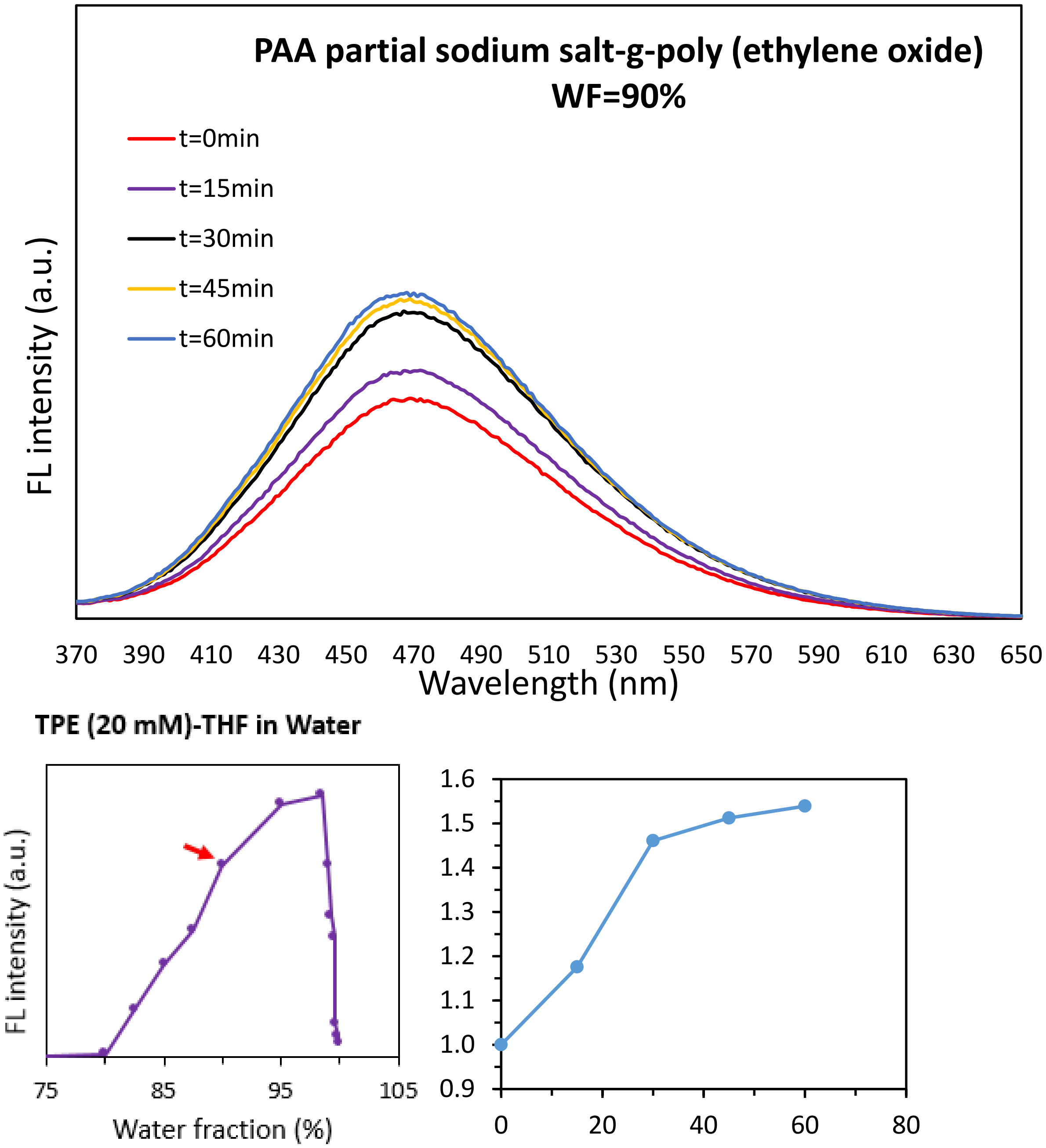

Figure S10. Change in FL spectra and relative FL intensity during the swelling process of SAP particles at WF= 90%.

Table S11. Calculations to support sink condition for TPE/THF in water

WF (%)	**Total volume of swelling environment** (μL)	**THF volume** (μL)	**(THF/Total) volume** (%)
85	2470	470	20%
90	2222	222	10%
95	2100	100	4.7%
98	2025	25	1.2%
99	2020	20	0.9%
99.3	2015	15	< 0.9%
99.5	2010	10	< 0.9%
99.7	2005	5	< 0.9%
99.8	2002.5	2.5	< 0.9%
99.9	2001	1	< 0.9%