Electronic Supporting Information

Emission Mechanism Understanding and Tunable Persistent Room Temperature Phosphorescence of Amorphous Nonaromatic Polymers

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Experimental Section

Materials: Acrylic acid (AA, 98%), acrylamide (AM, 99%), *N*-isopropyl acrylamide (NIPAM, 98%), sodium hydroxide (NaOH) and toluene were obtained from Adamas-Beta. Acetone, hydrochloric acid (HCl), tetrahydrofuran (THF) and dichloromethane (DCM) were obtained from shanghai Ling Feng Chemical Reagent Co., Ltd. *N*,*N*-dimethylformamide (DMF, spectroscopically pure) was purchased from TCI (Shanghai) Chemical Industry Co., Ltd. AA, acetone, THF and toluene were distilled before use. AM and NIPAM were recrystallized from chloroform and *n*-hexane, respectively. DCM was distilled from calcium hydride (CaH_2) under nitrogen immediately prior to use.

Instrumentation: ^1H and ^{13}C NMR spectra were measured on a Bruker ARX 400 NMR spectrometer using DMSO-d_6 or D_2O as solvent and tetramethylsilane (TMS) as internal standard. Weight-average molecular weights (M_w) and polydispersity index (PDI) of the polymers were estimated on a Waters gel permeation chromatography (GPC) system using $NaNO_3$ aqueous solution (0.1 M) as eluent. XRD measurements were conducted on powders and films with a D8 Advance diffractometer (Bruker, Germany) and a Cu Kα radiation source (λ = 1.5418 Å), at a scanning rate of 6 ^{o} min^{-1}. The X-ray tube voltage and current were set at 40 kV and 40 mA, respectively. The glass transition temperature (T_g) of the polymer powders and films were measured using DSC (Q2000, TA Instruments, New Castle, DE, USA) under nitrogen during the second heating cycles with a scan rate of 20 ^{o}C min^{-1}. Emission spectra were recorded by a PerkinElmer LS55 fluorescence spectrophotometer. Lifetimes were measured on an Edinburgh FLS920 fluorescence spectrometer. Quantum efficiencies of the solutions and solids were determined on a

Quantaurus-QY C11347–11 absolute PL quantum yield measurement system (Hamamatsu, Japan). The single crystal X-ray diffraction data of AM and NIPAM were collected on an Agilent Xcalibur and Gemini single-crystal X-ray diffractometer using the enhanced CuK X-ray source radiation (λ = 1.54184 Å) at 173 K in the ω scan mode.

Synthesis of Poly(acrylic acid) (PAA). PAA was synthesized via the isothermal precipitation polymerization. Briefly, into a 500 mL two-necked round bottom flask was placed AA (0.1 mol) and AIBN (1 mmol). The flask was evacuated under vacuum and flushed with nitrogen three times. Then distilled toluene (250 mL) was injected and the mixture was stirred at 70 ^{o}C for 5 h, during which white solids were precipitated out from the solvent. Afterwards, the mixture was cooled to room temperature and the solids were collected through filtration. After being dried in vacuum (60 ^{o}C, 24 h), the solids were dissolved in deionized water and dialyzed through a regenerated cellulose membrane tubing (MWCO = 2000) for 72 h. Finally, the dialyzed solution was freeze dried to yield white solids in 68.6% yield. M_w = 33 200, M_w/M_n = 1.3. ^{1}H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 12.26 (s, 1H, COOH), 3.34 (1H, CH), 1.73 (2H, CH_2); ^{13}C NMR (101 MHz, DMSO-d_6), δ (TMS, ppm): 181.12 (C=O), 46.24, 41.29.

Synthesis of Polyacrylamide (PAM). PAM was synthesized according to the similar procedures described above. THF instead of toluene was used as the polymerization media. White solids were obtained in 56.8% yield. M_w = 31 600, M_w/M_n = 3.0. ^{1}H NMR (400 MHz, D_2O), δ (TMS, ppm): 3.79, 1.89, 1.46, 1.03; ^{13}C NMR (101 MHz, D_2O), δ (TMS, ppm): 175.21, 41.73, 34.36, 21.59.

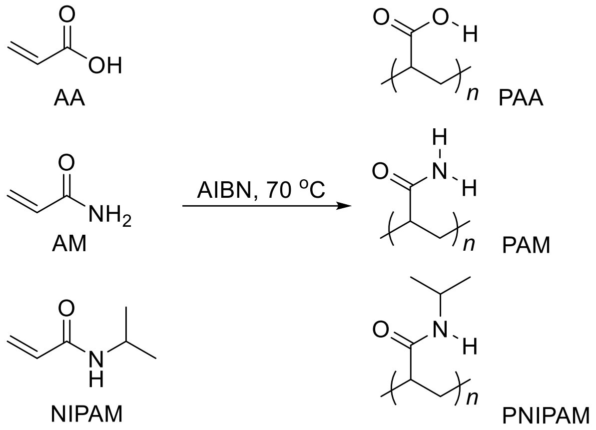
Synthesis of Poly(N-isopropyl acrylamide) (PNIPAM). M_w = 22 500, M_w/M_n = 1.2. PNIPAM was synthesized according to the similar procedures described above for the preparation of PAA, while THF was used as the solvent. Meanwhile, owing to the good solubility in THF, the crude PNIPAM was obtained by the rotary evaporation to remove the solvent. After dialysis and freeze-drying, white solids were obtained in 62.7% yield. ^{1}H NMR (400 MHz, D_2O), δ (TMS, ppm): 2.04, 1.45; ^{13}C NMR (101 MHz, D_2O), δ (TMS, ppm): 179.51, 41.50, 34.82.

Preparation of PAANa and PAACa powders. Aqueous NaOH (1 M) was slowly dropped into the aqueous PAA solution (1 M) under stirring until the pH was adjusted to 7.2. After freeze-drying for 72 h, white powders were received. PAACa salts were prepared by mixing the same volume of PAA (1 M) and $CaCl_2$ (0.5 M) solutions with subsequent lyophilization.

Preparation of PAMHCl powders. A 20 mL glass bottle containing PAM powders (0.5 g) was placed in a 100 mL beaker containing concentrated hydrochloric acid (12 M, 20 mL). The beaker was tightly sealed and placed in an oven for 48 h. The sample was taken out and dried in vacuum at 40 ^{o}C for 24 h.

Preparation of Polymer Films. Polymer powders (1 mmol) were added into DMF (2 mL, for PAA and PNIPAM) or water (2 mL, for PAM) and stirred overnight. The resulting solution (0.5 M) was then cast onto a glass plate by a stainless steel scraper and placed in an oven at 60 ^{o}C for 24 h. The resulting films were obtained for further characterization.

Cell Culture and Confocal Imaging. HCT116 cells were seeded in a glass bottom dish (35 mm dish with 20 mm bottom well) with McCoy’s5A containing 10% fetal bovine serum and 1% penicillin-streptomycin. The dish was cultured in a humidified incubator containing 5% CO_2 at 37 °C for 24 h, then the cells were stained with PAM/McCoy’s5A solution (500 μL, 1 M) for 1.5 h and washed three times with phosphate buffer solution (PBS). Afterwards, they were imaged using a laser scanning confocal microscopy (Leica SP8 STED 3X) at an excitation wavelength of 405 nm.



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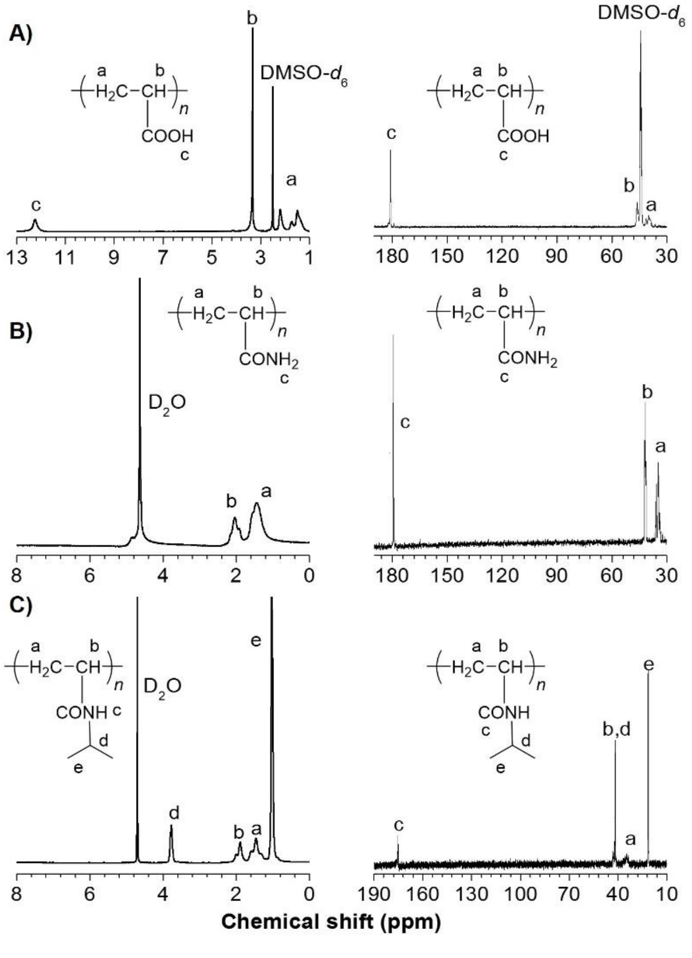

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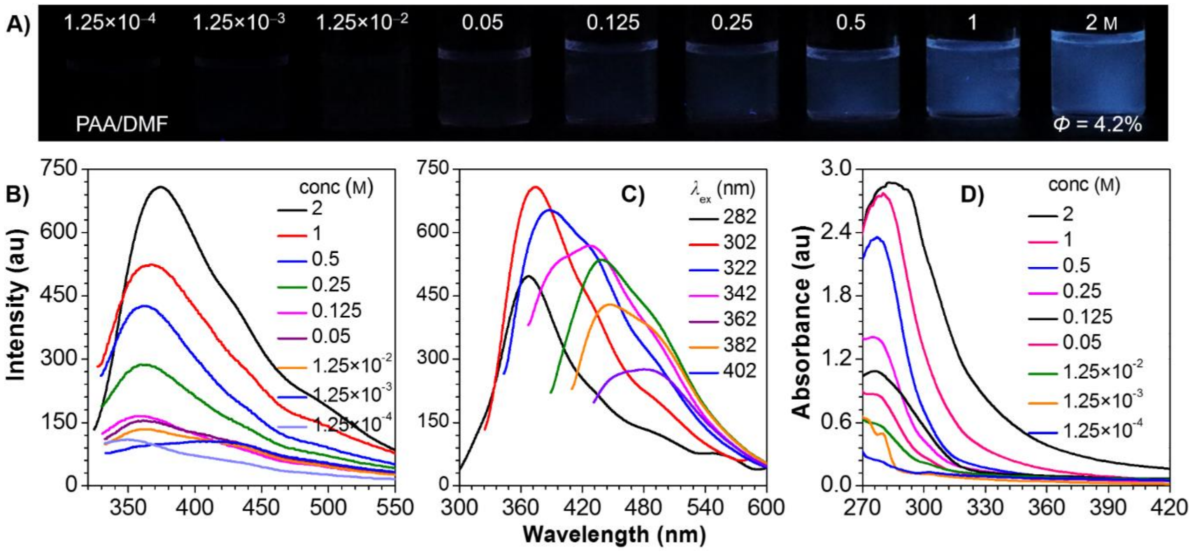
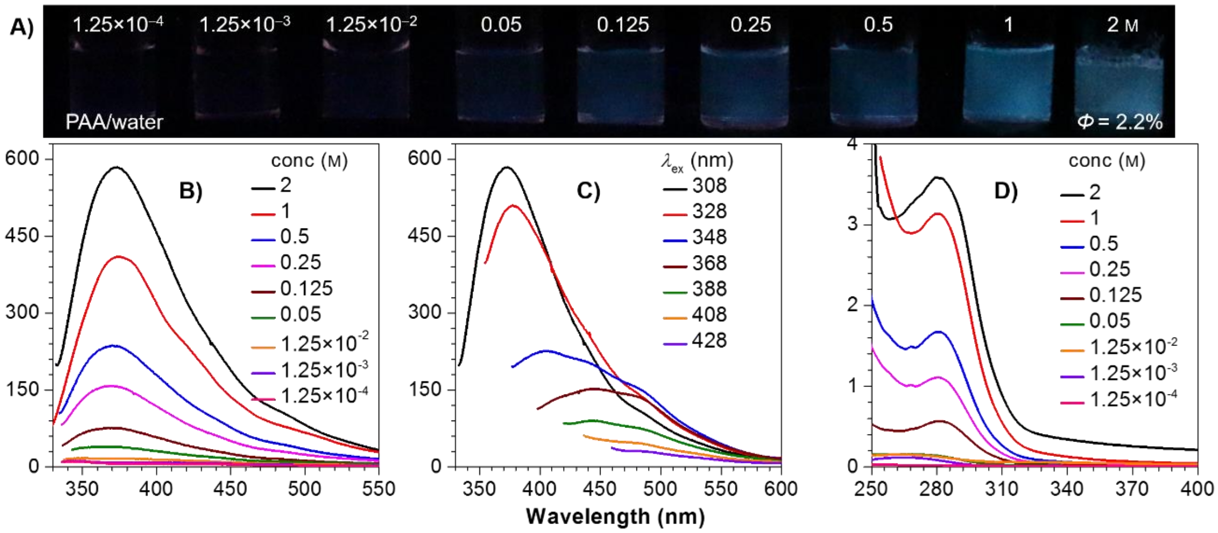


Fig. S2 (A) Photographs taken under 365 nm UV light and (B) emission spectra of PAA/DMF solutions at different concentrations (λ_{ex} = 302 nm). (C) Emission spectra of 2 M PAA/DMF with different λ_{ex}s. (D) Absorption of PAA/DMF solutions at different concentrations.



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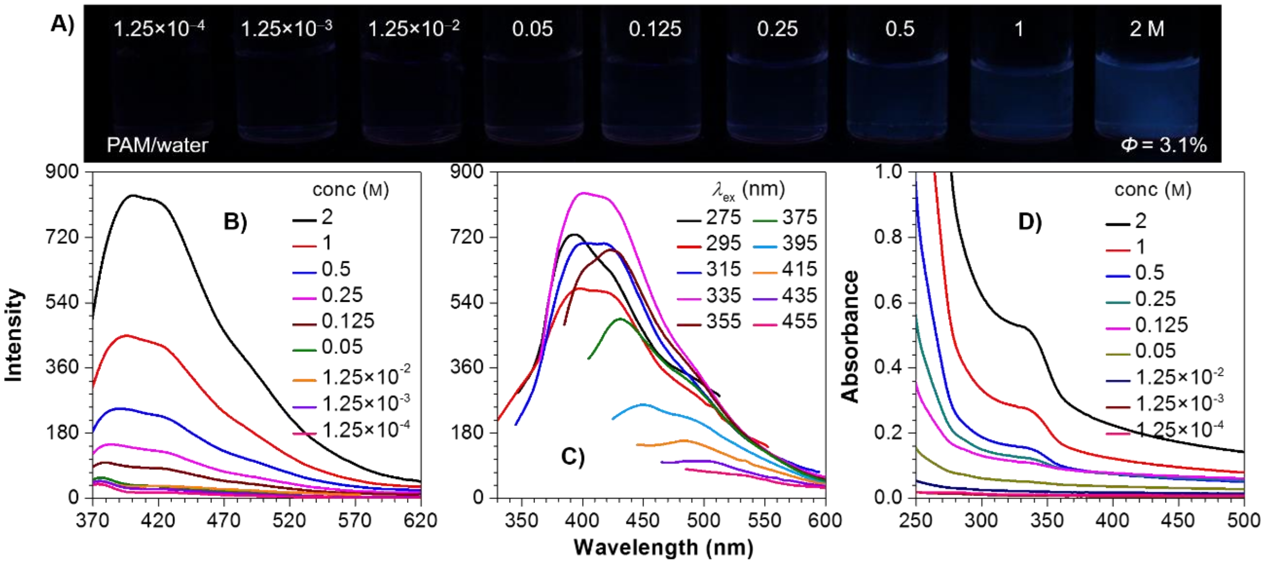


Fig. S4 (A) Photographs taken under 365 nm UV light and (B) emission spectra of PAM/water solutions at different concentrations (λ_{ex} = 335 nm). (C) Emission spectra of 2 M PAM/water with different λ_{ex}s. (D) Absorption of PAM/water solutions at different concentrations.

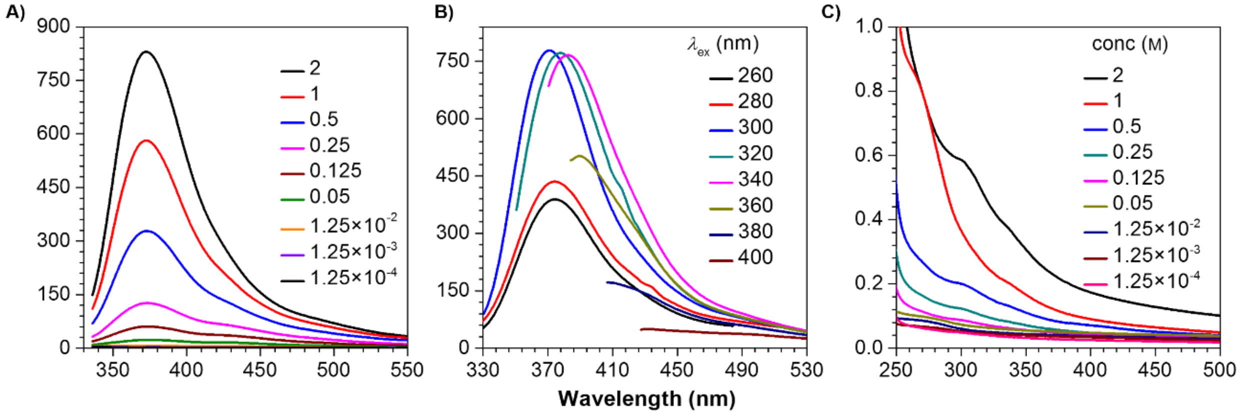


Fig. S5 PL spectra of (A) different PNIPAM/water solutions (λ_{ex} = 300 nm) and (B) 2 M aqueous solution with different λ_{ex}s. (C) Absorption of PNIPAM/water solutions at different concentrations.

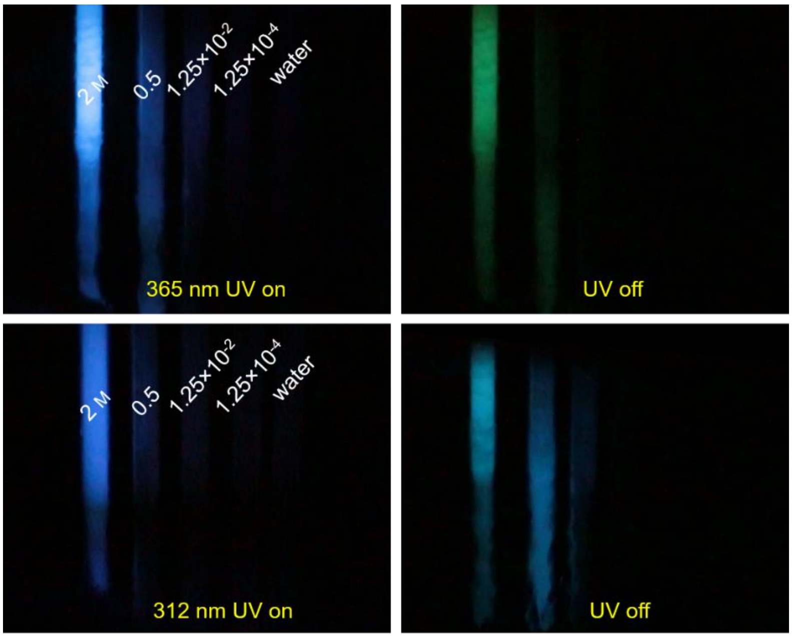


Fig. S6 Photographs of different PNIPAM/water solutions taken under 365 and 312 nm UV lights or after ceasing the irradiation at 77 K.

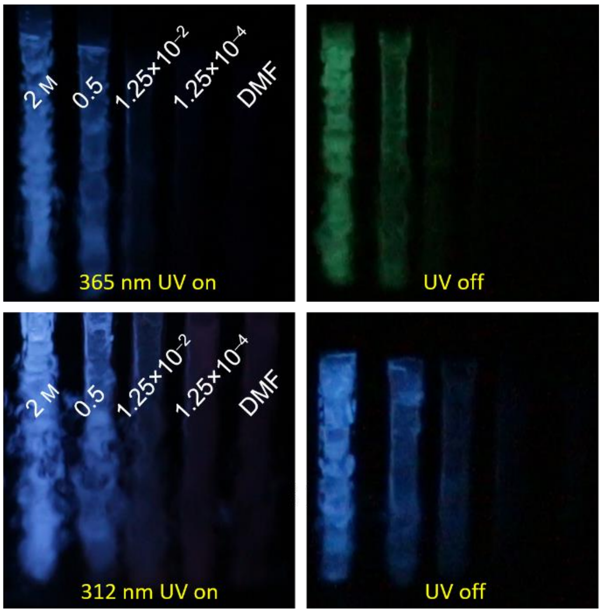


Fig. S7 Photographs of different PAA/DMF solutions taken under 365 and 312 nm UV lights or after ceasing the irradiation at 77 K.

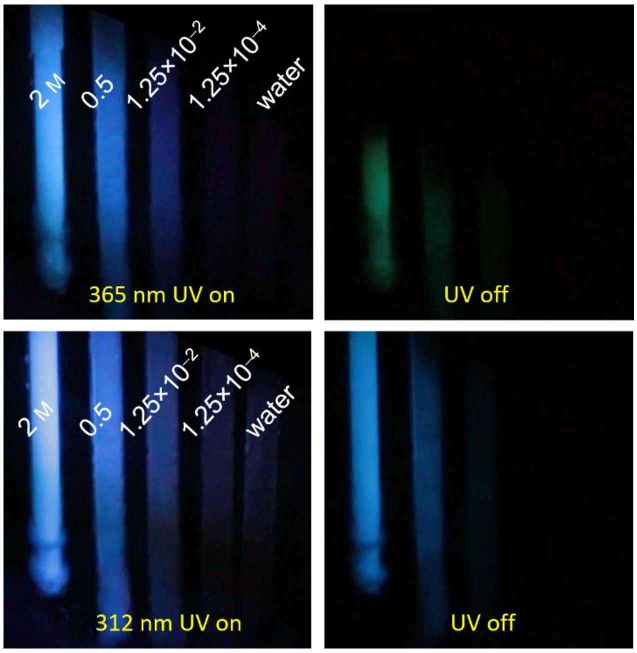


Fig. S8 Photographs of different PAM/water solutions taken under 365 and 312 nm UV lights or after ceasing the irradiation at 77 K.

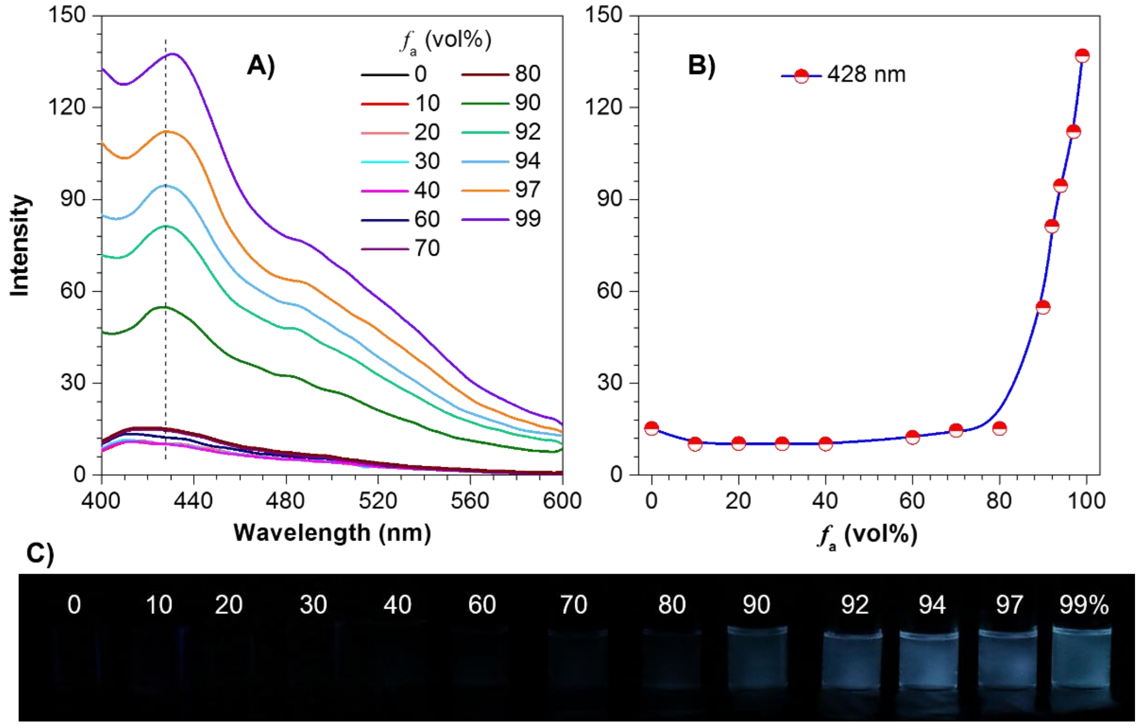


Fig. S9 (A) PL spectra, (B) peak intensities and (C) photographs taken under 365 nm UV light of PAA in water and water/acetone mixtures with different acetone fractions (f_as) (1.25×10^{-3} M, $\lambda_{ex} = 368$ nm).

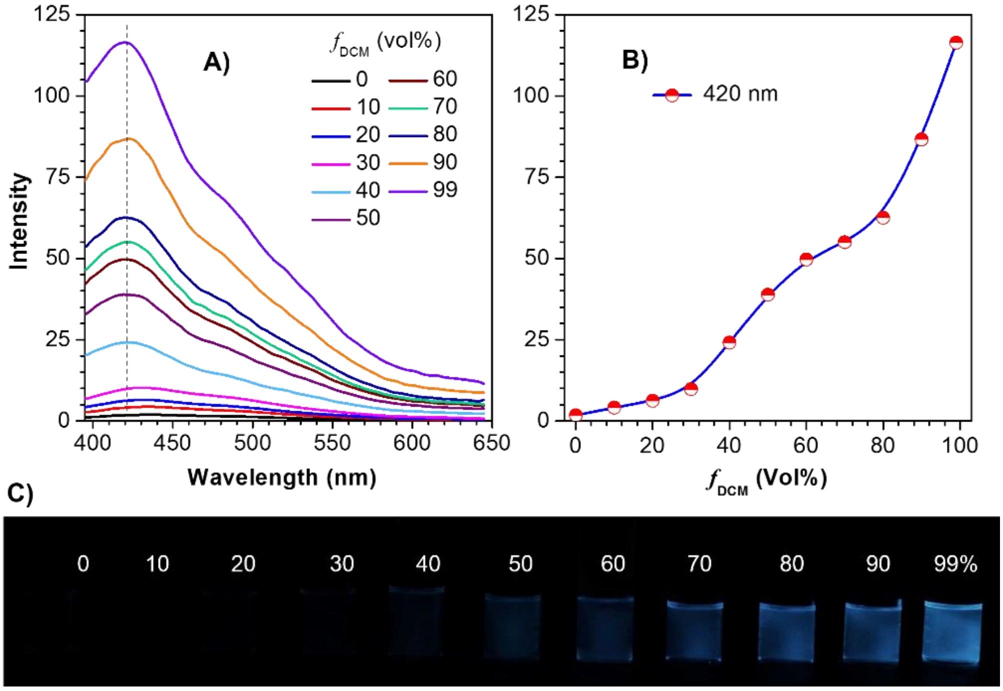


Fig. S10 (A) PL spectra, (B) peak intensities and (C) photographs taken under 365 nm UV light of PAA in DMF and DMF/DCM mixtures with different DCM fractions (f_{DCM}s) (1.25×10^{-4} M, λ_{ex} = 368 nm).

Table S1 Photophysical data of different samples of PAA, PAM and PNIPAM.[a]

Polymer	PAA	PAM	PNIPAM	PNIPAM-*p*	PAANa	PAMHCl
	$\lambda_{ex,o}/\lambda_{em,o}/\Phi$	$\lambda_{ex,o}/\lambda_{em,o}/\Phi$	$\lambda_{ex,o}/\lambda_{em,o}/\Phi$	$\lambda_{ex,o}/\lambda_{em,o}/\Phi$	$\lambda_{ex,o}/\lambda_{em,o}/\Phi$	$\lambda_{ex,o}/\lambda_{em,o}/\Phi$
	[nm]/[nm]/[%]	[nm]/[nm]/[%]	[nm]/[nm]/[%]	[nm]/[nm]/[%]	[nm]/[nm]/[%]	[nm]/[nm]/[%]
DMF solution	302/374/4.2	–	310/374/8.9	–	–	–
Aqueous solution	308/373/2.2	335/401/3.1	300/373/6.2	–	–	–
Powder	320/374/4.5	301/371/8.3	304/360/9.6	310/367	320/377/7.6	340/397/16.7
Cast film	330/398/5.7	332/377/13.7	306/366/12.4	–	–	–

[a] $\lambda_{ex,o}$ = optimal excitation wavelength; $\lambda_{em,o}$ = optimal emission wavelength; Φ = quantum efficiency.

Table S2 Summary of the RTP lifetimes of different samples.^{a}

Samples	τ_1 [ms]	A_1 [%]	τ_2 [ms]	A_2 [%]	τ [ms]	$\lambda_{ex,RTP}$ [nm]	$\lambda_{em,RTP}$ [nm]
PAA powder	4.7	27.2	41. 8	72.8	31.7	320	488
PAANa powder	7.2	10.8	139.1	89.2	124.9	320	478
PAA film	7.3	22.4	54.4	77.6	43.8	330	504
PAM powder	3.9	19.5	97.6	80.5	79.3	301	482
PAMHCl powder	17.2	24.1	116.9	75.9	92.8	340	488
PAM film	7.0	13.1	117.0	86.9	102.6	332	489
PNIPAM powder	5.2	18.9	89.4	81.1	73.5	280	479
PNIPAM/*p* powder	8.9	12.1	143.7	87.9	127.3	280	479

[a] All measurements were conducted at ambient conditions except PNIPAM and PNIPAM/*p* powders, which were carried out under nitrogen. $\lambda_{ex,RTP}$ = excitation wavelength used for the lifetime measurement; $\lambda_{em,RTP}$ = monitored emission wavelength. $\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.

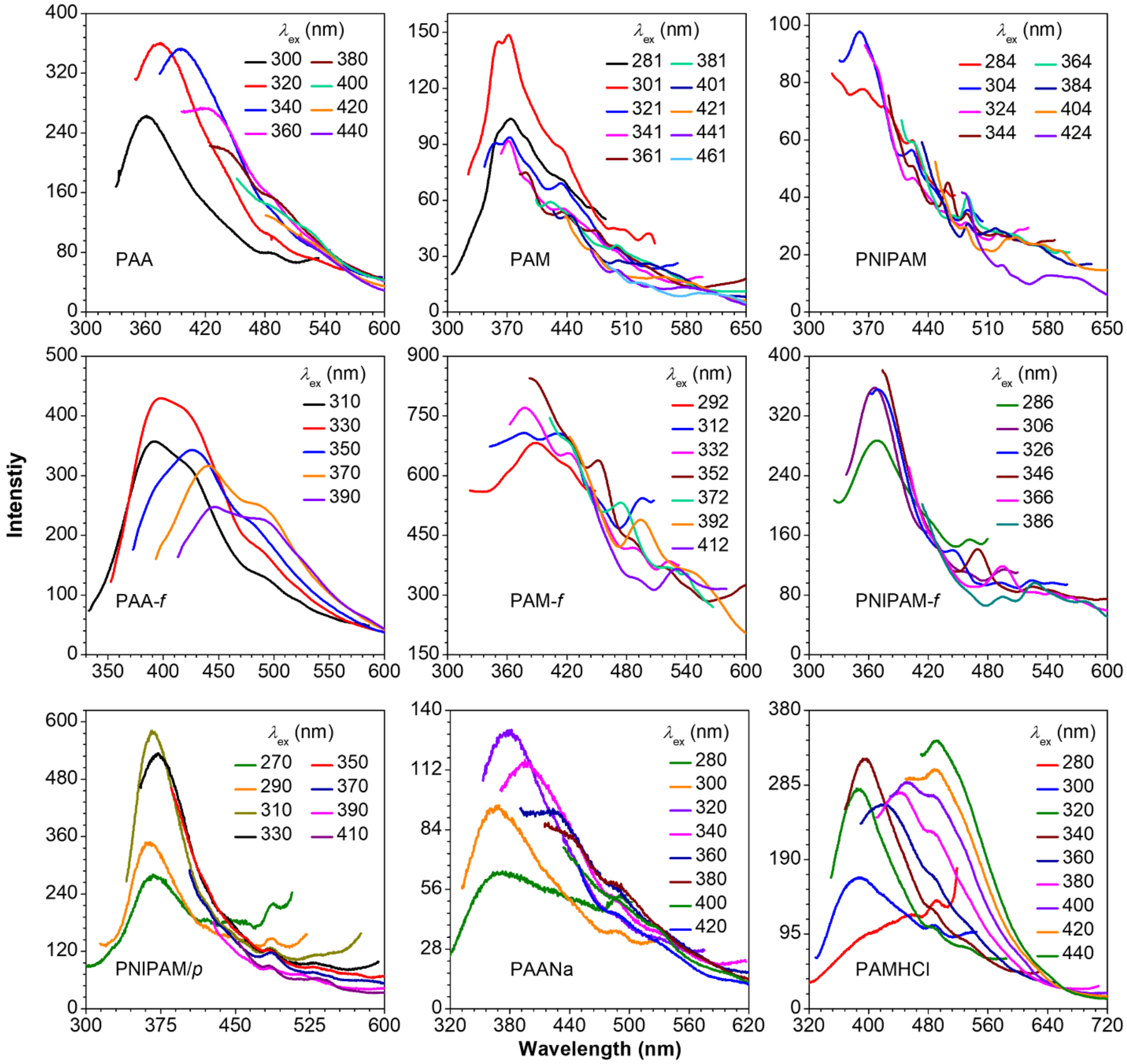


Fig. S11 Emission spectra of various solid powders and films (*f*) with different λ_{ex}s.

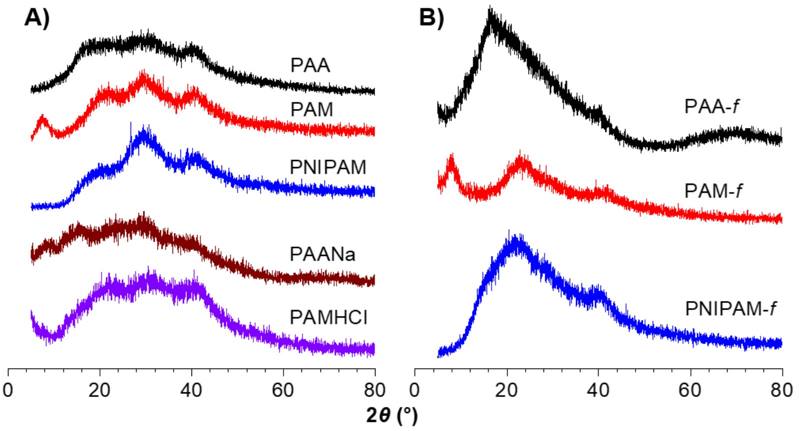


Fig. S12 X-ray diffraction (XRD) patterns of polymer (A) powders and (B) films.

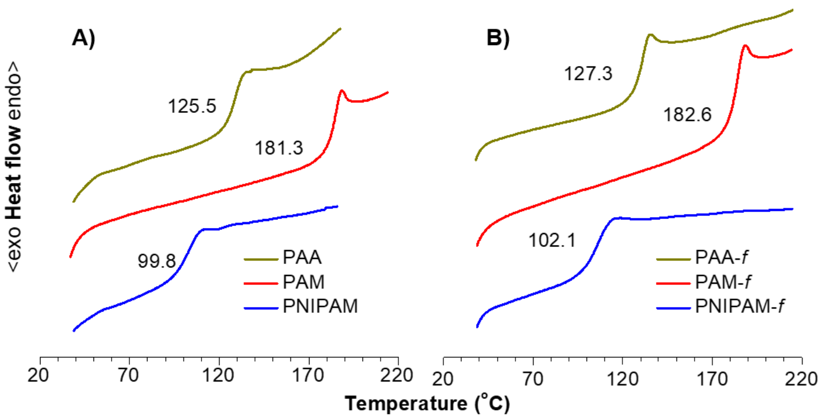


Fig. S13 DSC thermograms of polymer (A) powders and (B) films.

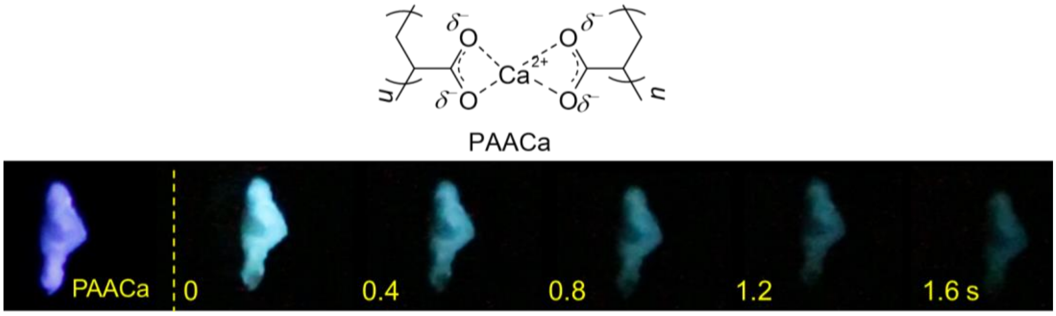
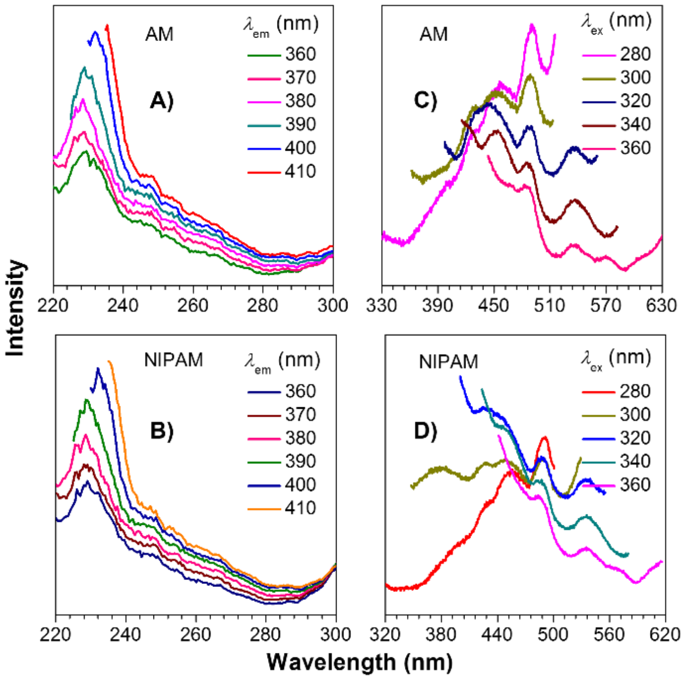


Fig. S14 Structure of PAACa and its photographs taken under 312 nm UV light or after ceasing the UV irradiation at ambient conditions.



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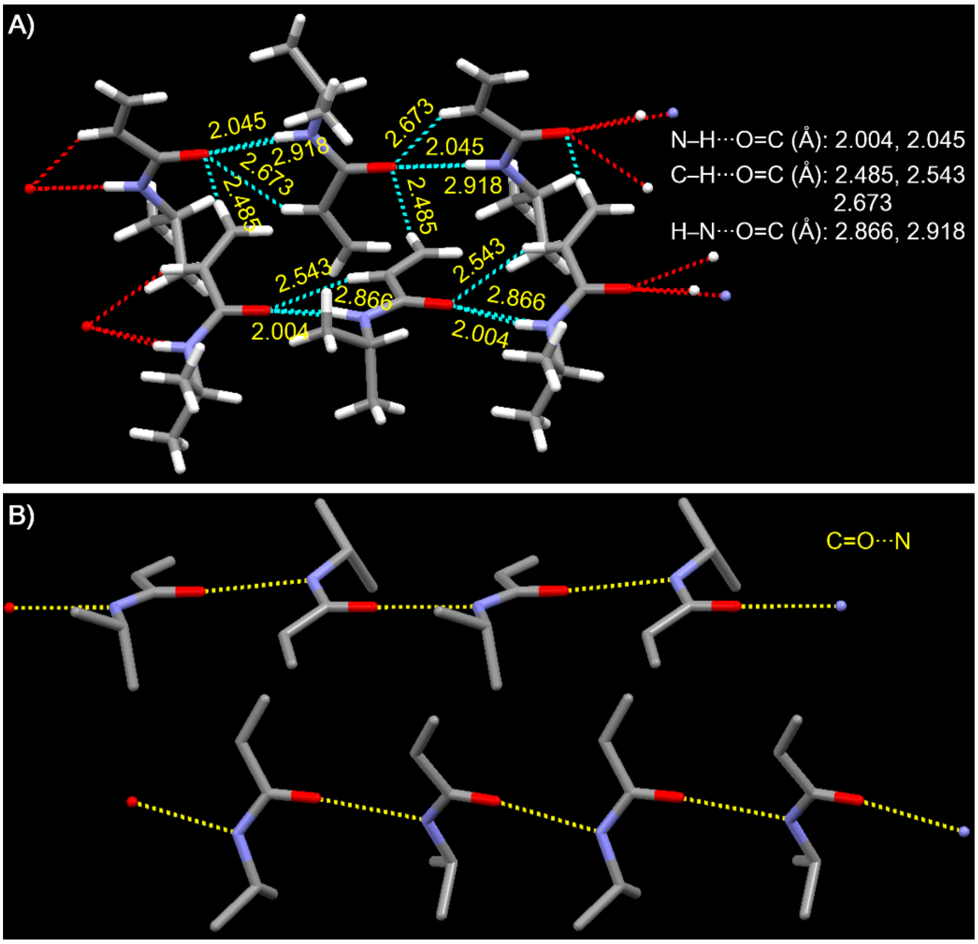

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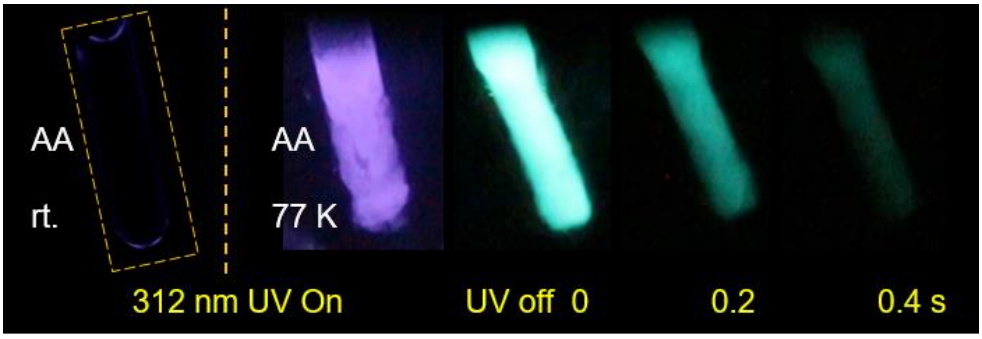

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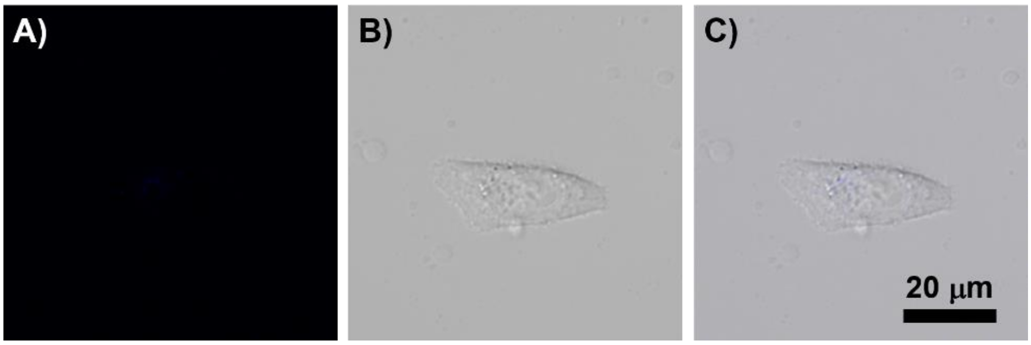

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