Supporting Information

Amide Cluster Induced and Hydrogen Bonding Regulated Luminescence of Linear Aliphatic Polyamide 1212 with Long Alkane Chain

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EXPERIMENTAL SECTION

Deconvolution of Amide I: The results are meaningless if the shape, number, position and full width at half maximum of the fitted peaks, the position of the baseline, etc. are not determined, and the investigators have done sufficient preliminary work for this research. It was finally determined that the absolute absorbance was deconvoluted in the region 1600 - 1700 cm-1 in a Gaussian peak pattern, which also avoided the problem of overlapping contributions from the flanks. There are three components in this region as shown in Figure S6: i) 1668 cm-1 (FWHM = 26 cm-1), attributed to free C=O; ii) 1640 cm-1 (FWHM = 27 cm-1), attributed to disordered C=O, and iii) 1631 cm-1 (FWHM = 17 cm-1) and 1616 cm-1 (FWHM = 15 cm-1).[1-4]

The content of ordered hydrogen bonded C=O (cOH), content of disordered hydrogen bonded C=O (cDH) and content of hydrogen bonded C=O (cH) are calculated from equation 1, 2 and 3 respectively.

$$c_{OH} = \frac{A_O}{A_F + A_O + A_D} \qquad (equ\ 1)$$

$$c_{DH} = \frac{A_D}{A_F + A_O + A_D} \qquad (equ\ 2)$$

$$c_{H} = \frac{A_O + A_D}{A_F + A_O + A_D} \qquad (equ\ 3)$$

where A_O is the area of the ordered hydrogen bonded C=O stretching vibrational absorption peak, A_D is the area of the disordered hydrogen-bonded C=O stretching vibration absorption peak, A_F is the area of the free C=O stretching vibration absorption peak.

PA1-PA7 Sample preparation: PA1-PA7 are all hot-pressing film with different post-treat thermal histories. All the films are unified and prepared by vacuum hot press machine (K001, China), and the preparation process is as follows: 0.5 g purified and dried PA 1212 granules were placed in the middle of the mold with a diameter of 25mm and a thickness of 1mm. With 1000kg pressure, the molding part was heated to 200 °C

under vacuum and kept for 5 min. Took out the prepared films and quenched in an ice-water bath for 3min. The quenched films were then annealed at 50°C, 70°C, 90°C, 100°C, 120°C, 140°C and 155°C for 2 hours, respectively, correspondingly named as P1 to P7.
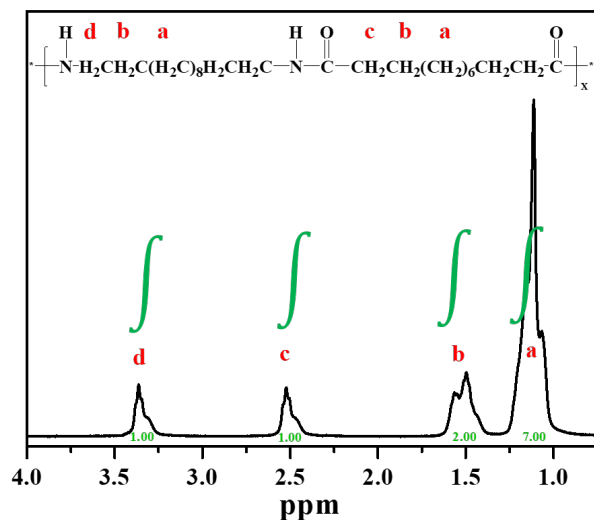
FIGURES AND TABLES

Figure S1. ^{1}H-NMR analysis of PA1212 after purification (in CF$_3$COOD).

^{1}H-NMR spectrum of PA1212 after purification is shown in Figure S1. The signal at 1.0~1.25ppm is assigned to the chemical shift of the methylene group (a) far from the amide group. The signal at around1.5 ppm is assigned to the chemical shift of β-H (b). The signals at 2.5 ppm and 3.3 ppm are assigned to the chemical shifts of α-H of diacid unit (c) and diamine unit (d), respectively. The integral area ratio of a:b:c:d is 7:2:1:1, which is exactly the same as the structure of PA 1212 shown in the repeating unit.
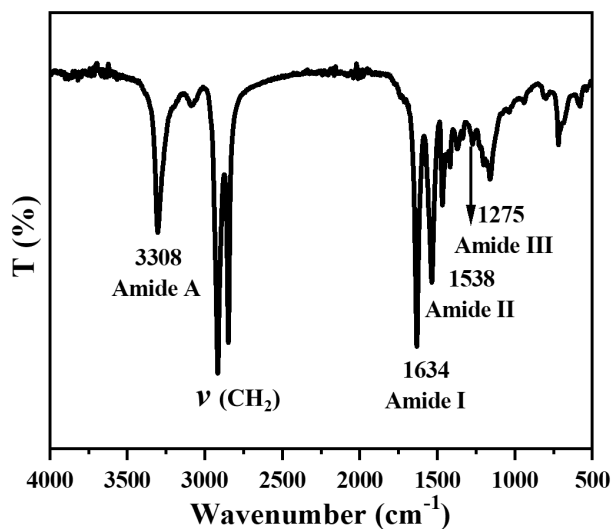
Figure S2. FT-IR spectrum of PA1212 film.

As shown in the FTIR spectrum of PA1212 (Figure S2), the characteristic absorption bands of polyamide are well located, including N-H stretching vibration band (Amide A, 3308 cm^{-1}), C=O stretching vibration band (Amide I, 1634 cm^{-1}), the coupling of in-plane C=O bending and C-N stretching vibration band (amide II, 1538 cm^{-1}), the C=O in-plane bending vibration band (Amide III, 1275 cm^{-1}) and CH$_2$ stretching vibration band (asymmetric and symmetric, 2850~2900 cm^{-1}).
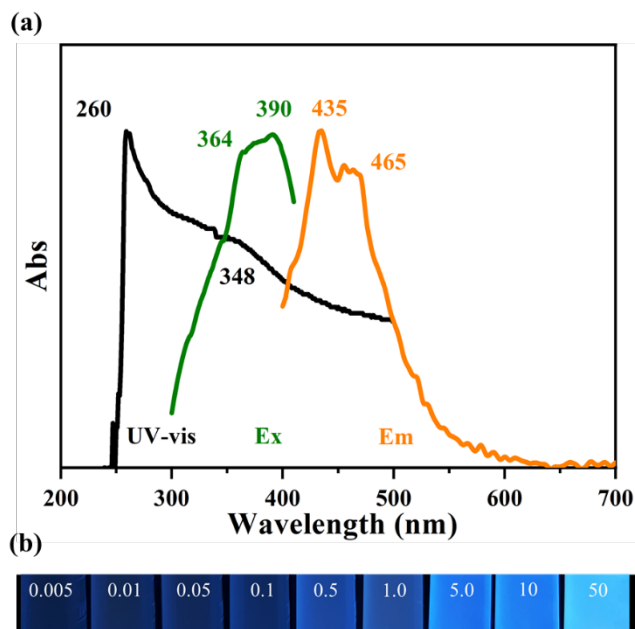
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Figure S3. (a) UV-vis absorption, excitation and emission spectra of PA1212 solution (TFA, c=1 mg/mL); (b) Photographs of different PA1212/TFA concentration solutions taken under 365nm UV light at room temperature.
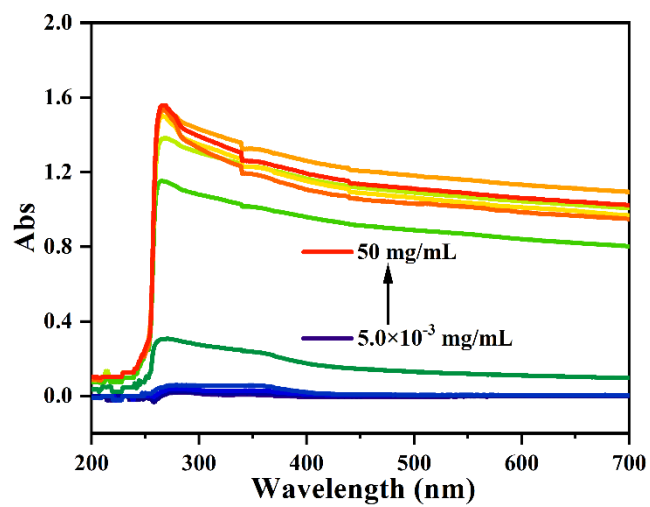
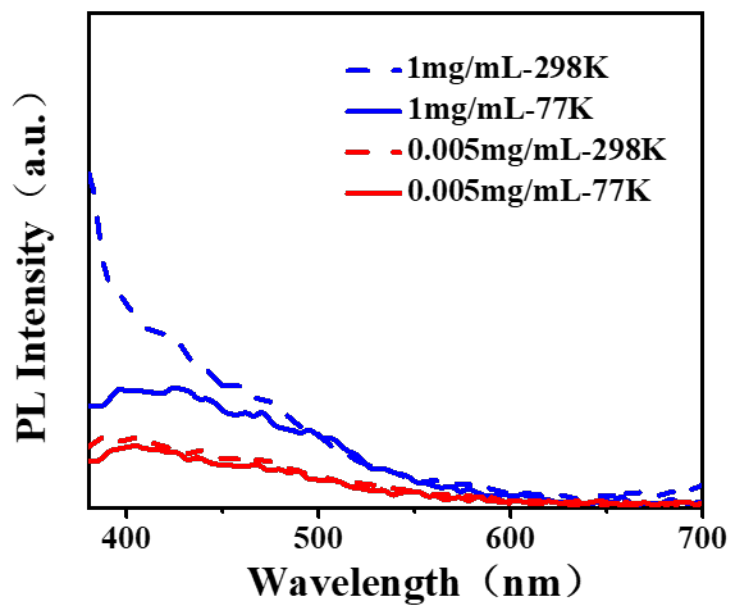**Figure S4.** UV-vis absorption spectra of PA1212 solution with different concentrations.

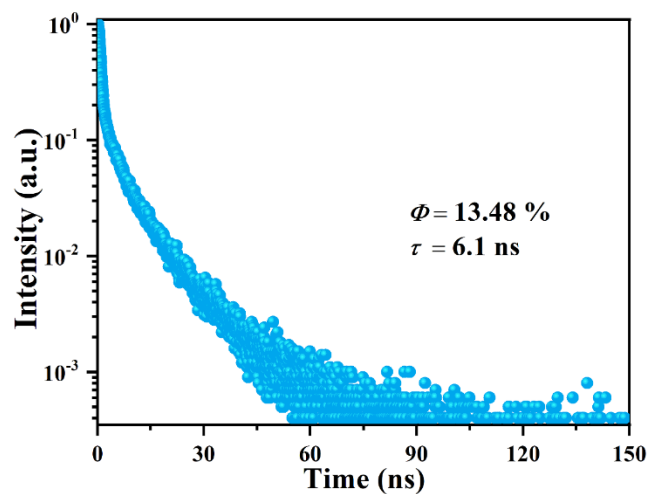**Figure S5.** Fluorescence emission spectra of PA1212/TFA solutions at different temperatures.

Figure S6. Fluorescence lifetime spectrum and quantum yield (*Φ*) of PA1212 film.
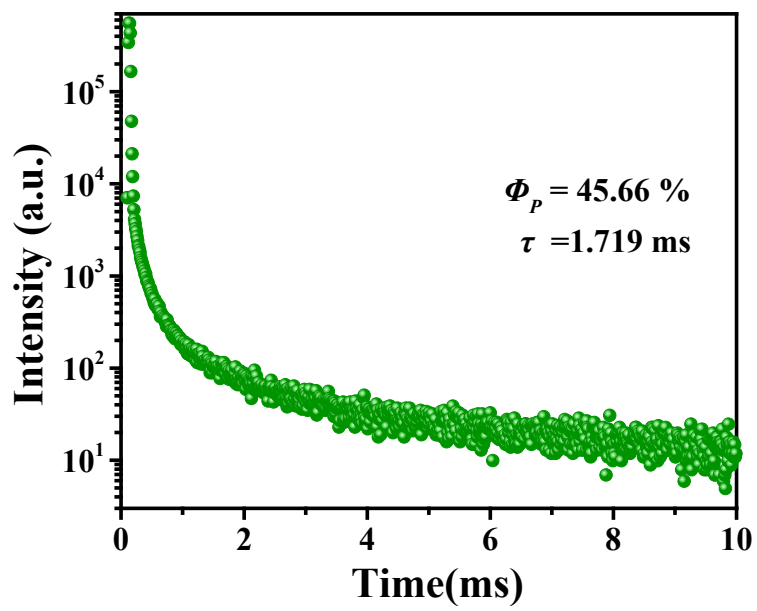
Φ_P = 45.66 %

τ =1.719 ms

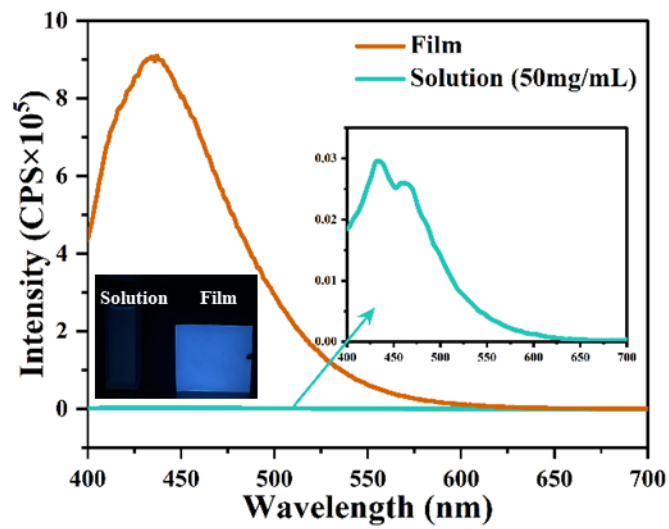**Figure S7.** Phosphorescence Lifetime spectrum and quantum yield (Φ) of PA1212 film.

Figure S8. Fluorescence spectra and fluorescent photographs (inserted) of PA1212 film and concentrated solution.
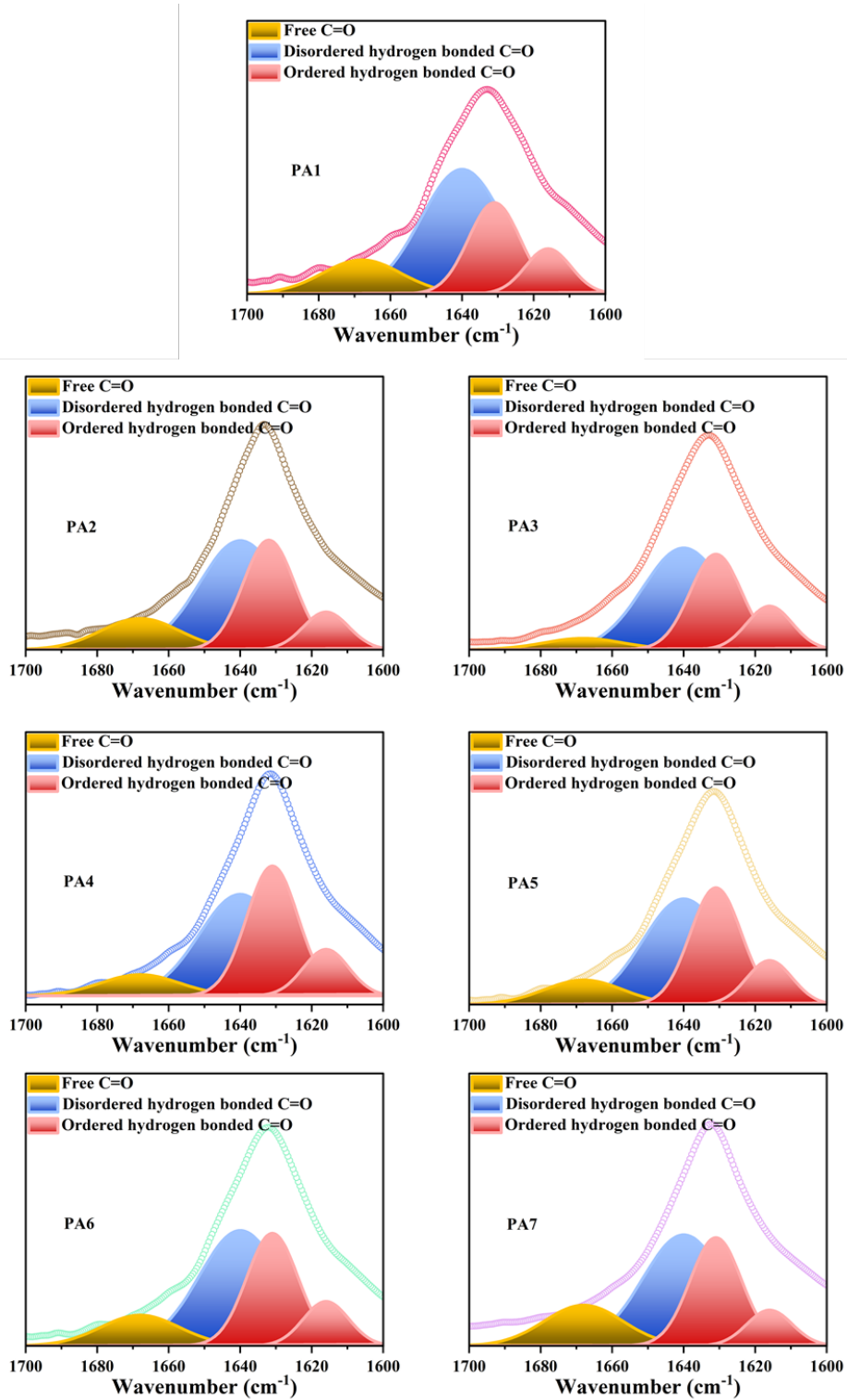
Figure S9. Deconvolution analysis of Amide I band (the stretching vibration of C=O) in FTIR of PA1212 films.
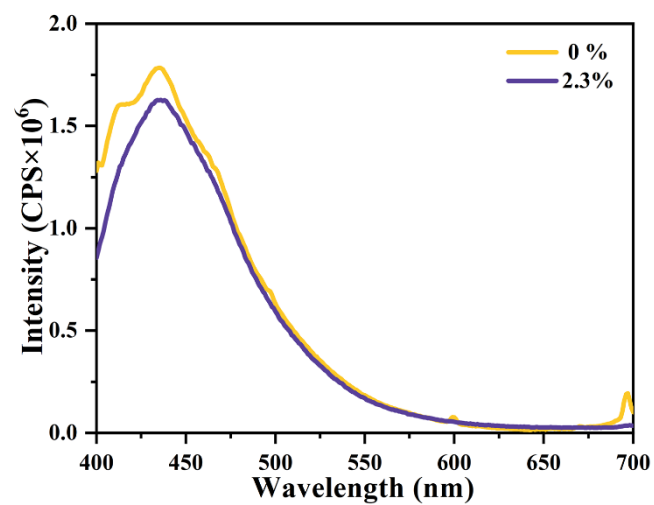
Figure S10. Fluorescence spectra of PA1212 films before and after water absorption.

Table S1. DSC and FT-IR data analysis results of PA1-PA7.

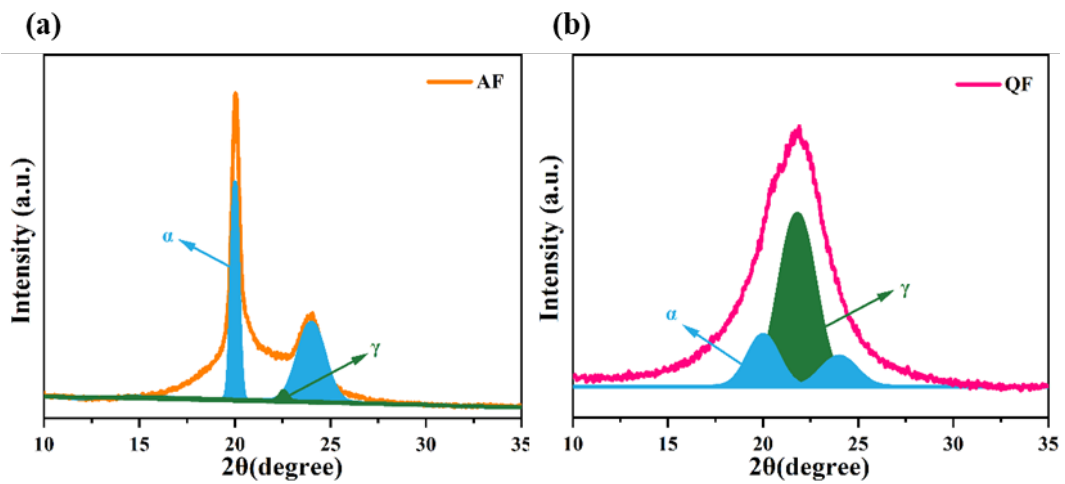| Sample	X_c [a] （%）	c_{OH}	c_{DH}	c_H
PA1	27.0	0.344	0.519	0.863
PA2	29.4	0.393	0.476	0.869
PA3	32.8	0.428	0.517	0.945
PA4	35.6	0.469	0.442	0.911
PA5	33.3	0.431	0.465	0.896
PA6	29.9	0.397	0.480	0.877
PA7	27.4	0.369	0.466	0.836

[a] Data obtained from the DSC, $\Delta H_m^0 = 292.2$ J/g.[5]

Figure S11. Schematic diagram of XRD split peaks (a) AF and (b) QF.

Table S2. XRD data results of AF and QF.[6]

Sample	2θ (°)	$d_{spacing}$[a] (nm)	Crystal form	Fraction (%)
QF	20.00	0.443	α	30
	24.00	0.371		
	21.80	0.407	γ	70
AF	20.00	0.443	α	98
	24.00	0.371		
	22.54	0.407	γ	2

a calculated by Bragg equation $2d\sin\theta=n\lambda$, where $n=1$, $\lambda=0.154$ nm
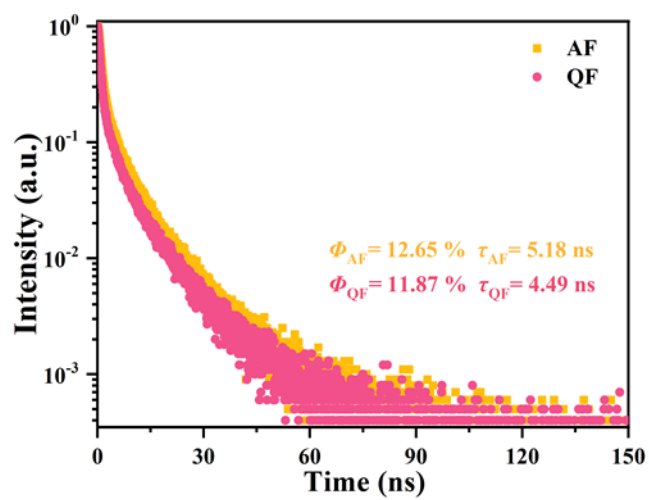
Figure S12. Fluorescence lifetime spectra and quantum yield (Φ) of AF and QF.
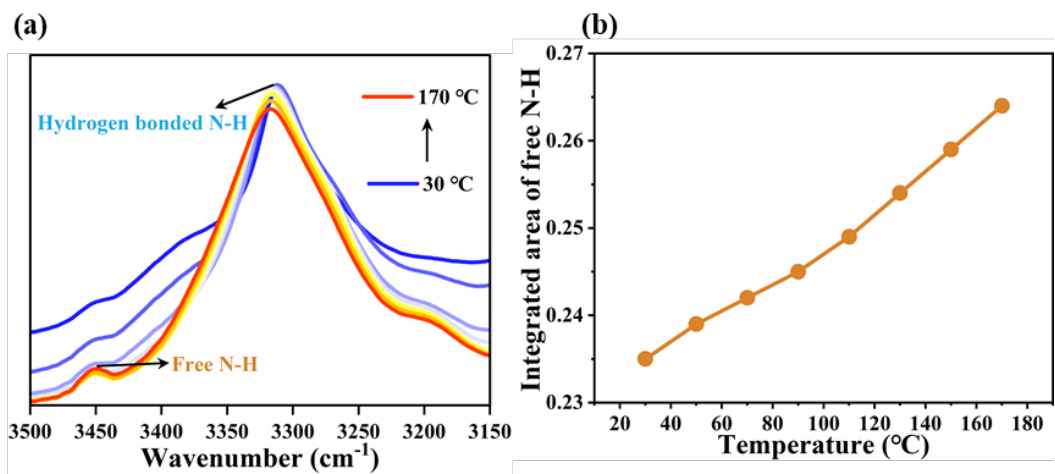
Figure S13. (a) Amide A region in the variable temperature infrared spectra of PA1212 film; (b) The integrated area of the free N-H stretching vibration at different temperatures.
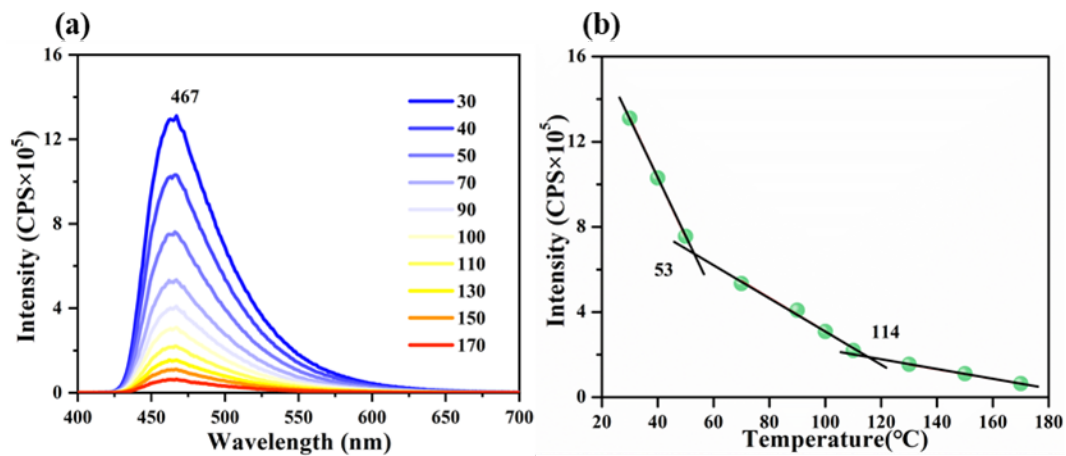
Figure S14. PA1212 films (a) variable temperature fluorescence emission spectra with a 385 nm filter and (b) the emission intensity at different temperatures (λ_{em} = 467 nm)
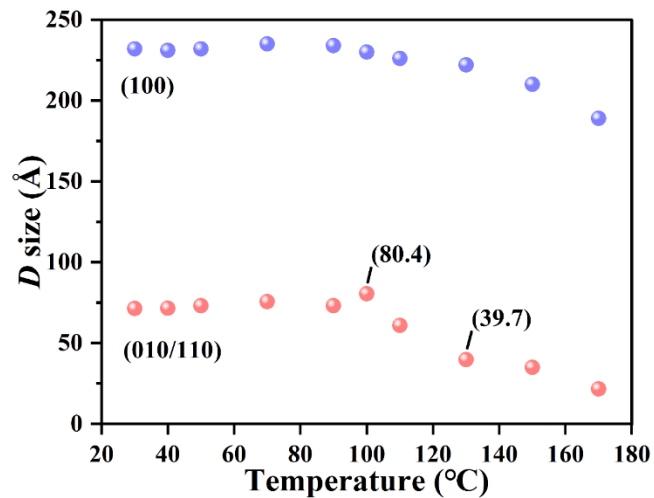
Figure S15. *D* size of (100) and (010/110) crystal planes at different temperatures of the PA1212 film.

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