

Electronic Supplementary Material (ESI) for RSC Advances
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Supporting Information

Thermally responsive AIE-active polyurethanes based on a tetraaniline derivative

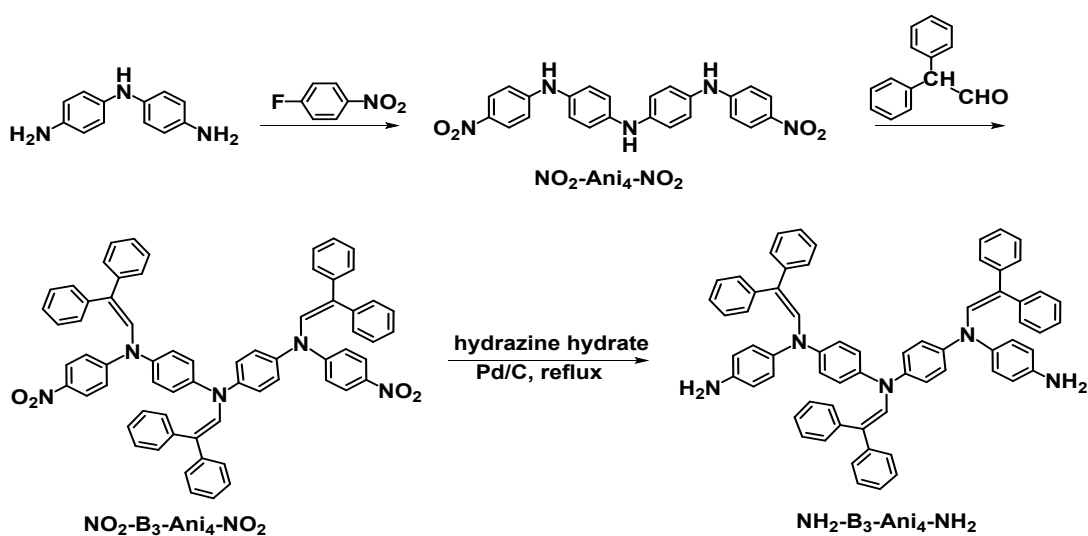
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1. Synthesis



Scheme S1 Synthetic route of $\text{NH}_2\text{-B}_3\text{-Ani}_4\text{-NH}_2$.

1.1 N,N-bis(4''-nitrophenyl)-4,4''-diaminodiphenylamine ($\text{NO}_2\text{-Ani}_4\text{-NO}_2$)

4,4'-Diaminodiphenylamine sulfate hydrate (9.22 g, 31 mmol) and triethylamine (9.95 g, 98 mmol) were dissolved in 50 mL of dimethyl sulfoxide (DMSO) at room temperature, and 4-fluoro-nitrobenzene (11.03 g, 78 mmol) was added in sequence. The mixture was stirred at 90 °C for 72 h under nitrogen atmosphere to avoid amine oxidation. After the mixture was cooled to room temperature and poured into stirred water, the resulting precipitates were collected and purified by reprecipitation from tetrahydrofuran (THF) to give desired $\text{NO}_2\text{-Ani}_4\text{-NO}_2$.

NO₂ as brown powder (11.62 g, yield 85%). FTIR (KBr, cm⁻¹): 3356 (N-H); 2975, 2913, 2848 (C-H, Ar); 1600, 1297 (NO₂); 1113 (C-N); 831, 750, 694 (C-H, Ar). ¹H NMR (600 MHz, DMSO-d₆), δ, ppm: 9.12 (s, 2H, C-NH), 8.22 (s, H, C-NH), 8.04 (d, 4H, Ar-H), 7.16-7.10 (m, 8H, Ar-H), 6.90 (d, 4H, Ar-H). MS (MALDI-TOF): m/z: 440.9 (M⁺ calcd 441.1).

1.2 N,N''-bis[(4''-nitrophenyl)-N,N',N''-tris(2,2-diphenyl-vinyl)-4,4'-diaminodiphenylamine (NO₂-B₃-Ani₄-NO₂)

NO₂-Ani₄-NO₂ (0.882 g, 2 mmol), camphorsulfonic acid (0.02 g, 0.08 mmol) and diphenyl acetaldehyde (1.177 g, 6 mmol) were dissolved in THF (30 mL), and the resulting mixture was heated to reflux for 24 h under nitrogen atmosphere with stirring. Then the solvent was removed by rotary evaporation, and the left crude product was purified by recrystallization from ethyl acetate (EA) to give **NO₂-B₃-Ani₄-NO₂** as red powder (1.70 g, yield 87%). FTIR (KBr, cm⁻¹): 3058, 2920, 2853 (C-H, Ar); 1586, 1311 (NO₂); 1502 (C=C); 1113 (C-N); 840, 750, 699 (C-H, Ar). ¹H NMR (600 MHz, DMSO-d₆), δ, ppm: 8.08 (d, 4H, Ar-H), 7.13-7.34 (m, 30H, Ar-H), 6.87 (d, 8H, Ar-H), 6.78 (d, 4H, Ar-H), 6.55-6.60 (m, 3H, CH=C). MS (MALDI-TOF): m/z: 975.3 (M⁺ calcd 975.3).

1.3 N,N''-bis(4''-aminophenyl)-N,N',N''-tris(2,2-diphenylvinyl)-4,4'-diaminodiphenylamine (NH₂-B₃-Ani₄-NH₂)

NO₂-B₃-Ani₄-NO₂ (1.0 g, 1.02 mmol) and 10% Pd/C (0.1 g) were dispersed into ethyl alcohol, and added into the three-neck flask with magnetic stirring under nitrogen atmosphere. Then 10 mL hydrazine hydrate was added dropwise into the flask. After it was stirred and refluxed for 24 h, the mixture was filtered to remove Pd/C, then the filtrate was collected and cooled to room temperature to separate out the product **NH₂-B₃-Ani₄-NH₂** as yellow powder after dried in vacuo at 50 °C (0.83 g, yield 89%). FTIR (KBr, cm⁻¹): 3291, 3045 (NH₂); 1500 (C=C); 1256 (C-N); 830, 764, 697 (C-H, Ar). ¹H NMR (600 MHz, DMSO-d₆), δ, ppm: 7.30-7.00 (m, 30H, Ar-H), 6.85 (s, 3H, CH=C), 6.57-6.40 (m, 16H), 4.84 (s, 4H, NH₂). MS (MALDI-TOF): m/z: 915.3 (M⁺ calcd 915.4).

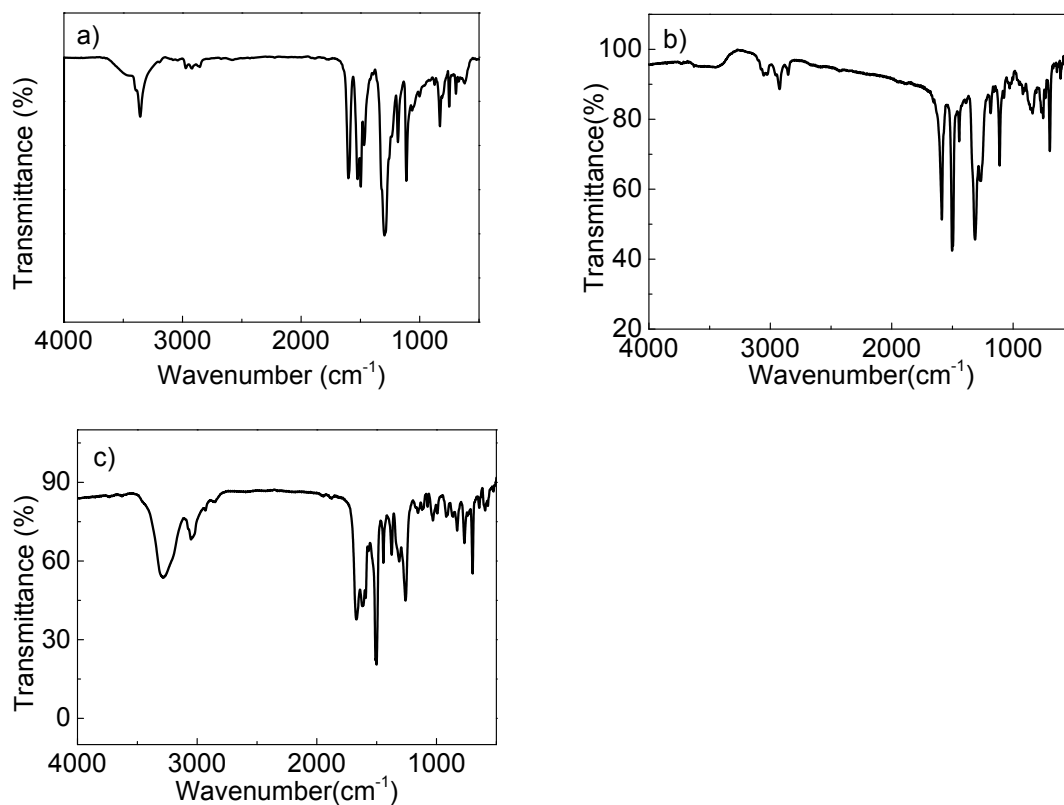


Fig. S1 FTIR spectra of a) $\text{NO}_2\text{-Ani}_4\text{-NO}_2$; b) $\text{NO}_2\text{-B}_3\text{-Ani}_4\text{-NO}_2$; c) $\text{NH}_2\text{-B}_3\text{-Ani}_4\text{-NH}_2$.

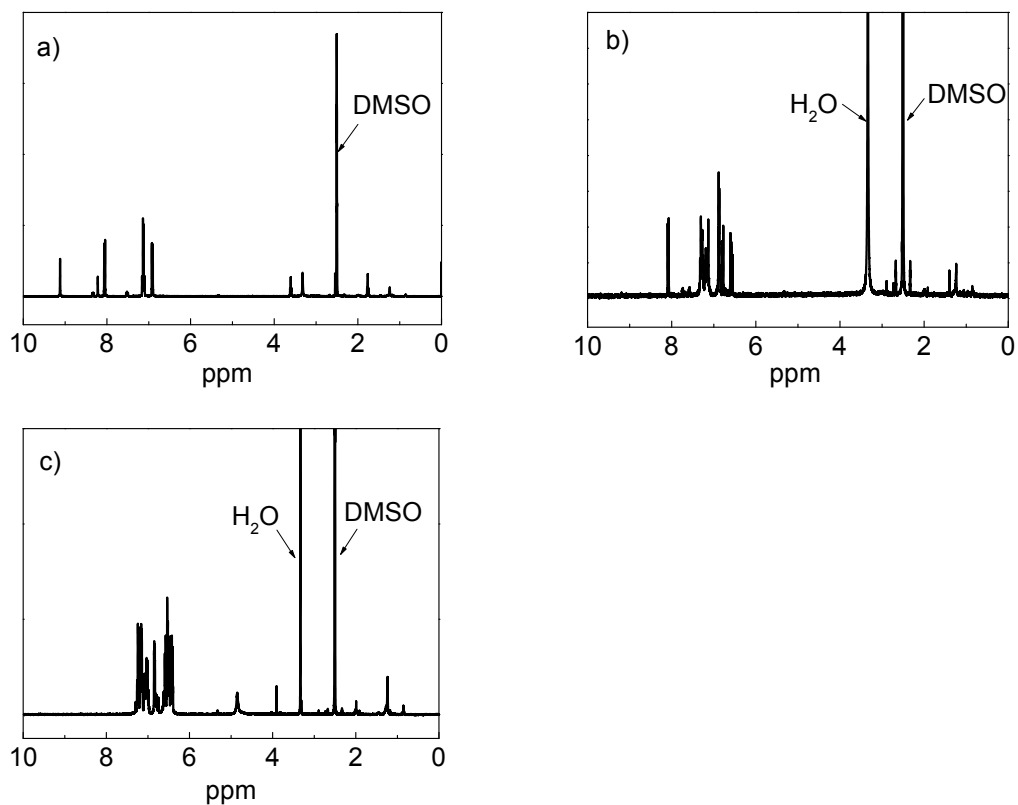


Fig. S2 $^1\text{H-NMR}$ spectra of a) $\text{NO}_2\text{-Ani}_4\text{-NO}_2$; b) $\text{NO}_2\text{-B}_3\text{-Ani}_4\text{-NO}_2$; c) $\text{NH}_2\text{-B}_3\text{-Ani}_4\text{-NH}_2$.

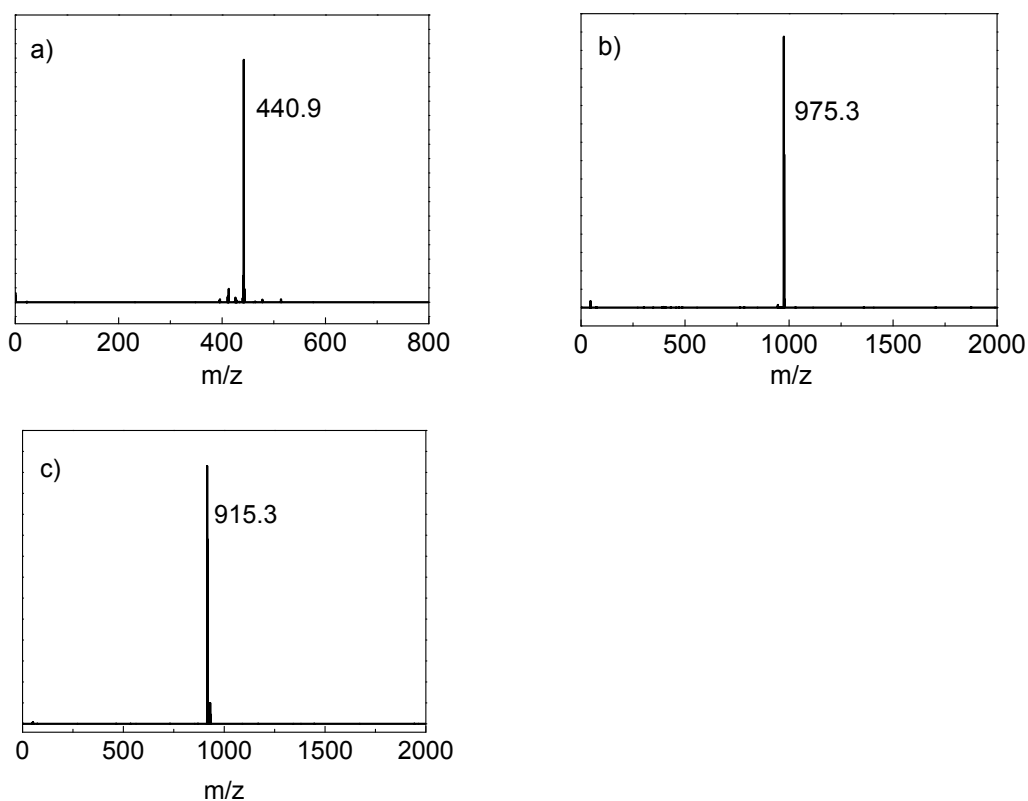


Fig. S3 MALDI MS spectra of a) $\text{NO}_2\text{-Ani}_4\text{-NO}_2$; b) $\text{NO}_2\text{-B}_3\text{-Ani}_4\text{-NO}_2$; c) $\text{NH}_2\text{-B}_3\text{-Ani}_4\text{-NH}_2$.

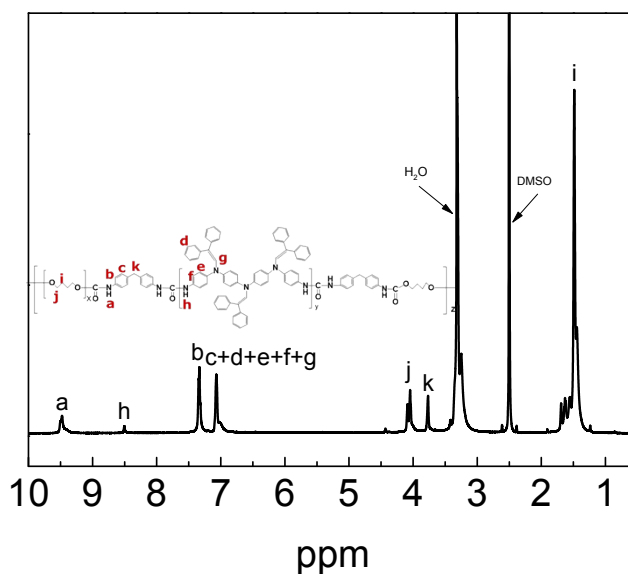


Fig. S4 $^1\text{H-NMR}$ spectrum of PU-211.

2. UV spectrometric method

Standard $\text{NH}_2\text{-B}_3\text{-Ani}_4\text{-NH}_2$ solutions with concentrations ranged from 0.001 mg/mL to 0.02 mg/mL were prepared by volumetric flasks. Then the UV spectra of $\text{NH}_2\text{-B}_3\text{-Ani}_4\text{-NH}_2$ solutions were showed in Fig. S5 a). Since the peak at 350 nm was ascribed to the characterized benzene group of $\text{NH}_2\text{-B}_3\text{-Ani}_4\text{-NH}_2$, it was selected to be a standard peak to

measure the mass concentrations of $\text{NH}_2\text{-B}_3\text{-Ani}_4\text{-NH}_2$ in three polyurethanes. As described in Figure S5 b), the absorption peak intensity at 350 nm was in proportion to the mass concentration of $\text{NH}_2\text{-B}_3\text{-Ani}_4\text{-NH}_2$. Then the Equation S1 could be obtained by fitting the above experimental data, in which c was the $\text{NH}_2\text{-B}_3\text{-Ani}_4\text{-NH}_2$ mass concentration in polyurethane solution and A was the UV absorbance of the corresponding polyurethane solution. By measuring the UV absorbances of three polyurethane solutions which have a same solution concentration of 3.0 mg/mL, $\text{NH}_2\text{-B}_3\text{-Ani}_4\text{-NH}_2$ mass concentrations of three polyurethanes could be calculated with Equation S1.

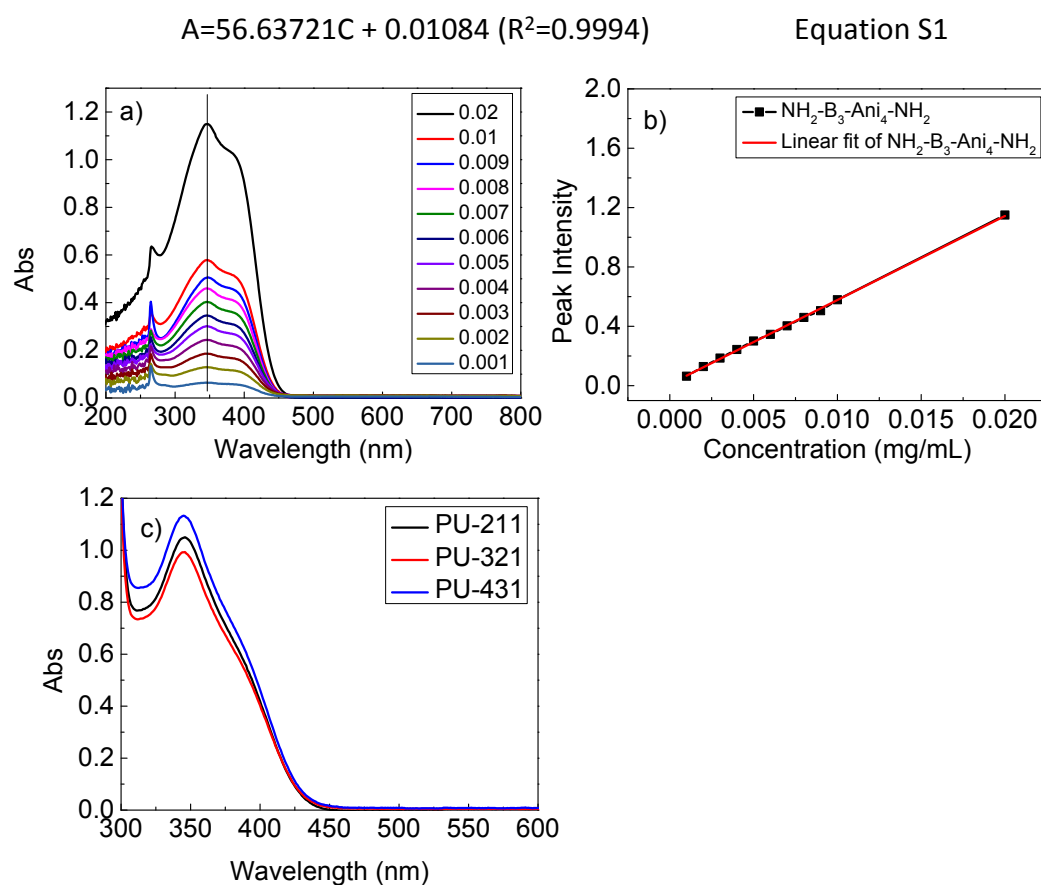


Fig. S5 a) UV spectra of $\text{NH}_2\text{-B}_3\text{-Ani}_4\text{-NH}_2$ at different concentration; b) Plot of UV peak intensity and $\text{NH}_2\text{-B}_3\text{-Ani}_4\text{-NH}_2$ solution concentration; c) UV-vis absorption spectra of three polyurethanes, concentration: 3.0 mg/mL.

Table S1. Mass fraction of $\text{NH}_2\text{-B}_3\text{-Ani}_4\text{-NH}_2$ in the three modified polyurethanes.

Polyurethane	UV absorbance	Experimental mass fraction (wt%)	Theoretical mass fraction (wt%)
PU-211	1.05	0.61	0.51
PU-321	0.99	0.58	0.51
PU-431	1.13	0.66	0.51

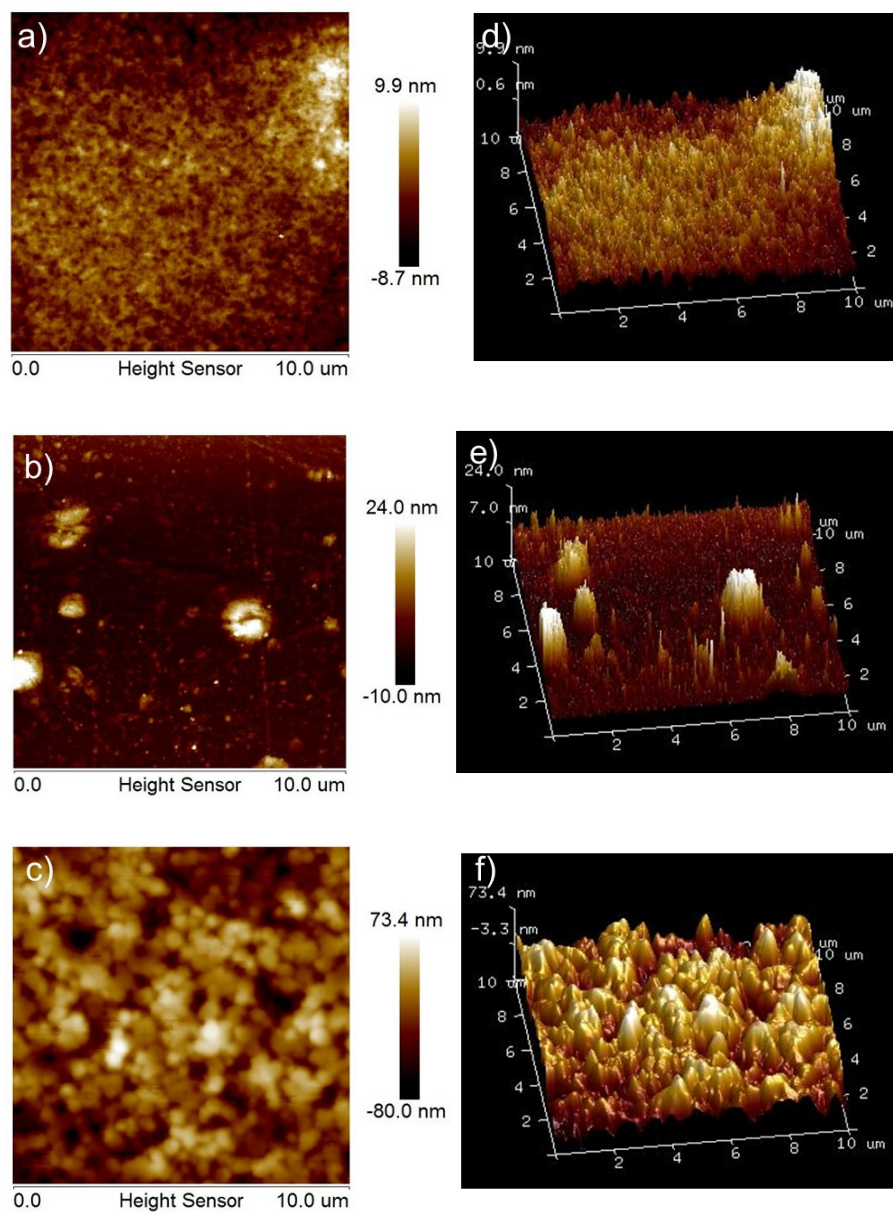


Fig. S6 AFM images of PU-211 thin films prepared by mixed solutions of different water fractions: (a), (b) and (c) are high contrast images at water fraction=0%, 40% and 80%, respectively; (d), (e) and (f) are the corresponding 3D high contrast images of (a), (b) and (c), respectively.