

Supporting Information for

Stimuli-Responsive Supramolecular Materials: Photo-Tunable Properties and Molecular Recognition Behavior

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Experimental Section

Materials

4-Vinylbenzyl chloride (VBC; Aldrich) was distilled from CaH_2 under reduced pressure. Propargyl bromide (80% in toluene, stabilized with MgO) was obtained from Alfa. All solvents were purchased from TEDIA (USA) and distilled over CaH_2 prior to use. Commercially available reagents were obtained from Sigma–Aldrich or Showa and used as received.

Propargyl thymine

A mixture of thymine (10.0 g, 80.0 mmol) and K_2CO_3 (16.3 g, 118 mmol) in DMF (250 mL) was stirred for 3 h and then cooled to 0 °C. Propargyl bromide (7.27 mL, 96.0 mmol) was added dropwise and then the reaction mixture was stirred for 24 h. After filtering off the salts and evaporating the solvent, the residue was purified through column chromatography (EtOAc/*n*-hexane, 2:1) to give a pale-yellow powder (10.5 g, 80%). ^1H NMR (500 MHz, CDCl_3 , δ , ppm): 9.21 (br, 1H, NH), 7.28 (s, 1H, thymine H-6), 4.56 (d, 2H, CH_2 of propargyl), 2.48 (t, 1H, CH), 1.97 (s, 3H, CH_3). ^{13}C NMR (500 MHz, CDCl_3 , δ , ppm): 164.0, 150.4, 138.3, 111.5, 76.2, 75.2, 36.5, 12.1.

11-Azidoundecanoic acid (Az-acid)

NaN_3 (1.50 g, 23.1 mmol) and 11-bromoundecanoic acid (5.30 g, 19.2 mmol) were placed in a two-necked reaction flask equipped with a condenser. DMSO (200 mL) was added and then the mixture was stirred at room temperature for 20 h. The solids were filtered off and the solution partitioned between EtOAc (100 mL) and saturated aqueous NaHCO_3 (100 mL); the organic phase was washed with D.I. water (3×100 mL), dried (MgSO_4), and concentrated through rotary evaporation to give a white solid. (4.20 g, 96%) ^1H NMR (500 MHz, CDCl_3 , δ , ppm): 3.25 (t, 2H, CH_2N_3), 2.34 (t, 2H, $\text{CH}_2\text{CO}_2\text{H}$), 1.54–1.66 (m, 4H, $\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$), 1.22–1.39 [m, 12H, $(\text{CH}_2)_6$], 0.93 (t, 3H, CH_3). ^{13}C NMR (500 MHz, CDCl_3 , δ , ppm): 180.1, 51.4, 34.0, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8, 26.7, 24.6.

4-(Phenyldiazenyl)phenyl 11-azidoundecanoate (Azo-Az)

A solution of Az-acid (5.00 g, 22.0 mmol) was heated under reflux in SOCl₂ (25 mL) for 1 h. Unreacted SOCl₂ was then evaporated under reduced pressure and the residue dissolved in dry THF (20 mL). This solution was added dropwise to a solution of **4-phenylazophenol** (3.63 g, 18.3 mmol) and Et₃N (2.19 g, 21.6 mmol) in dry THF (60 mL) under a N₂ atmosphere and then the mixture was stirred overnight. After filtration, the filtrate was concentrated and the residue dissolved in DCM. This solution was washed with D.I. water (3×) and dried (MgSO₄). The crude product was purified through reprecipitation into water two times to afford a yellow solid (5.97 g, 80%). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 7.95 (d, 2H, ArH), 7.90 (d, 2H, ArH), 7.51 (m, 2H, ArH), 7.47 (d, 2H, ArH), 7.24 (d, 1H, ArH), 3.25 (t, 2H, CH₂N₃), 2.59 (t, 2H, CH₂COO), 1.77 (tt, 2H, CH₂CH₂COO), 1.59 (m, 2H, CH₂CH₂COO), 1.22–1.39 [m, 12H, (CH₂)₆]. ¹³C NMR (500 MHz, CDCl₃, δ, ppm): 171.9, 152.8, 152.5, 131.0, 129.1, 124.0, 122.8, 122.2, 51.4, 34.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8, 26.7, 24.6.

Azo-T

A solution of Azo-Az (1.00 g, 2.46 mmol), propargyl thymine (0.800 g, 5.00 mmol), and PMDETA (50 μL) in dry DMF (40 mL) was subjected to three freeze/pump/thaw cycles. The flask was filled with N₂ and Cu(I)Br (30 mg) was quickly added. The mixture was stirred at 40 °C for 24 h and then the solvent was evaporated under reduced pressure. The residue was dissolved in DCM, washed with D.I. water, and purified through column chromatography (EtOAc/*n*-hexane, 1:4) to give a yellow powder (1.27 g, 90%) ¹H NMR (500 MHz, CDCl₃, δ, ppm): 8.41 (br, 1H, NH), 7.95 (d, 2H, ArH), 7.90 (d, 2H, ArH), 7.64 (s, 1H, thymine H-6), 7.55–7.41 (m, 4H, ArH), 7.33 (s, 1H, triazole), 7.24 (d, 2H, ArH), 4.93 (s, 2H, ArCH₂N), 4.31 (t, 2H, CH₂CH₂N), 2.58 (t, 2H, CH₂COO), 1.88 (s, 3H, thymine CH₃), 1.75 (tt, 2H, CH₂CH₂COO), 1.59 (m, 2H, CH₂CH₂COO), 1.22–1.39 [m, 12H,

(CH₂)₆]. ¹³C NMR (500 MHz, CDCl₃, δ, ppm): 171.9, 163.7, 152.7, 152.5, 150.6, 150.2, 142.0, 140.2, 131.1, 129.0, 124.0, 123.3, 122.8, 122.2, 111.2, 50.6, 43.0, 34.5, 30.2, 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 26.4, 24.9. ESI-MS [M + Na]⁺: calcd, *m/z* 594.28; found, 594.28 (the ESI mass spectrum is displayed in Fig. S8).

Prop-2-ynyl 4-(6-acetamidopyridin-2-ylamino)-4-oxobutanoate (SA-DAP)

A solution of 4-oxo-4-(prop-2-ynyloxy)butanoic acid (2.84, 18.2 mmol) in SOCl₂ (20 mL) was heated under reflux and then concentrated under vacuum distillation. The generated acid chloride was then mixed with *N*-(6-aminopyridin-2-yl)acetamide (3.30 g, 21.8 mmol) and Et₃N (1.65 mL) in dry THF (50 mL). When the reaction was complete (TLC), the mixture was filtered and the filtrate partitioned between DCM and saturated NaHCO₃. The organic phase was dried (MgSO₄) and concentrated. The residue was purified through column chromatography (EA) and dried under vacuum to give a white powder (4.1 g, 79%). ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm): 10.12 (s, 1H, NH), 10.06 (s, 1H, NH), 7.69 (m, 3H, ArH), 4.69 (d, 2H, CH₂COO), 3.53 (s, 1H, CH), 2.71 (t, 2H, CH₂CONH), 2.63 (t, 2H, CH₂COO), 7.24 (d, 2H, ArH), 4.93 (s, 2H, ArCH₂N), 4.31 (t, 2H, CH₂CH₂N), 2.10 (s, 3H, CH₃). ¹³C NMR (500 MHz, DMSO-*d*₆, δ, ppm): 172.6, 171.6, 170.2, 151.0, 140.6, 109.4, 78.9, 78.1, 52.1, 30.8, 28.4, 24.1. ESI-MS [M + Na]⁺: calcd, *m/z* 312.10; found, 312.10 (the ESI mass spectrum is displayed in Fig. S9).

PVBC homopolymer

VBC (3.05 g, 20.0 mmol), benzoyl peroxide (41.8 mg, 0.200 mmol), and TEMPO (32.2 mg, 0.260 mmol) were charged in a reaction flask. After degassing through three freeze/pump/thaw cycles, the mixture was heated at 95 °C for 3 h under vacuum and then at 120 °C until the required molecular weight had been achieved. The mixture was quickly cooled to room temperature and diluted with THF. The solid that precipitated from MeOH was dried under vacuum overnight. ¹H NMR (500

MHz, CDCl₃, δ , ppm): 7.04 (br, 2H, ArH), 6.48 (br, 2H, ArH), 4.52 (br, 2H, CH₂Cl), 1.70 (br, 2H, CH₂), 1.38 (br, 2H, CH₂). ¹³C NMR (500 MHz, CDCl₃, δ , ppm): 145.8, 135.6, 128.5, 46.5, 44.0, 40.5.

PVBaz

NaN₃ (1.00 g, 15.4 mmol) was added to a solution of PVBC (1.64 g, 10.6 mmol of VBC repeating units) in DMF (80 mL) and then the mixture was stirred at 60 °C for 48 h. The solvent was evaporated under reduced pressure and the residue dissolved in DCM. The solution was washed with D.I. water (3 \times), dried (MgSO₄), concentrated, and precipitated into MeOH to afford a pale-yellow powder (1.58 g, 96%), ¹H NMR (500 MHz, CDCl₃, δ , ppm): 6.98 (br, 2H, ArH), 6.47 (br, 2H, ArH), 4.25 (br, 2H, CH₂N₃), 1.69 (br, 2H, CH₂), 1.41 (br, 2H, CH₂). ¹³C NMR (500 MHz, CDCl₃, δ , ppm): 145.8, 133.4, 128.6, 54.7, 44.1, 40.5.

PVB-DAP

A solution of PVBaz (0.500 g, 3.10 mmol of N₃), SA-DAP (1.21 g, 4.18 mmol), and Cu(I)Br (9.00 mg, 0.0630 mmol) in DMF (60 mL) was subjected to three freeze/pump/thaw cycles. PMDETA (10 μ L) was added and the flask was filled with N₂. The mixture was stirred at room temperature for 24 h and then was passed through a short column of neutral aluminum oxide, followed by dialysis with 0.5 M HCl and MeOH to remove the catalyst. The crude product was precipitated into MeOH to give an off-white powder (0.57g, 75%). ¹H NMR (500 MHz, CDCl₃, δ , ppm): 10.28 (br, 1H, NH), 10.21 br, 1H, NH), 8.15 (br, 1H, triazole), 7.63 (br, 3H, ArH), 6.91 (br, 2H, ArH), 6.41 (br, 2H, ArH), 5.45 (br, ArCH₂N), 5.08 (br, 2H, CH₂N₃), 2.68 (t, 2H, CH₂CONH), 2.55 (t, 2H, CH₂COO), 2.10 (br, 3H, CH₃), 1.69 (br, 2H, CH₂), 1.41 (br, 2H, CH₂). ¹³C NMR (500 MHz, CDCl₃, δ , ppm): 173.1, 171.9, 170.5, 150.7, 150.5, 142.8, 141.1, 133.7, 128.2, 125.5, 109.3, 57.6, 52.7, 40.3, 40.2, 30.8, 28.4, 24.1.

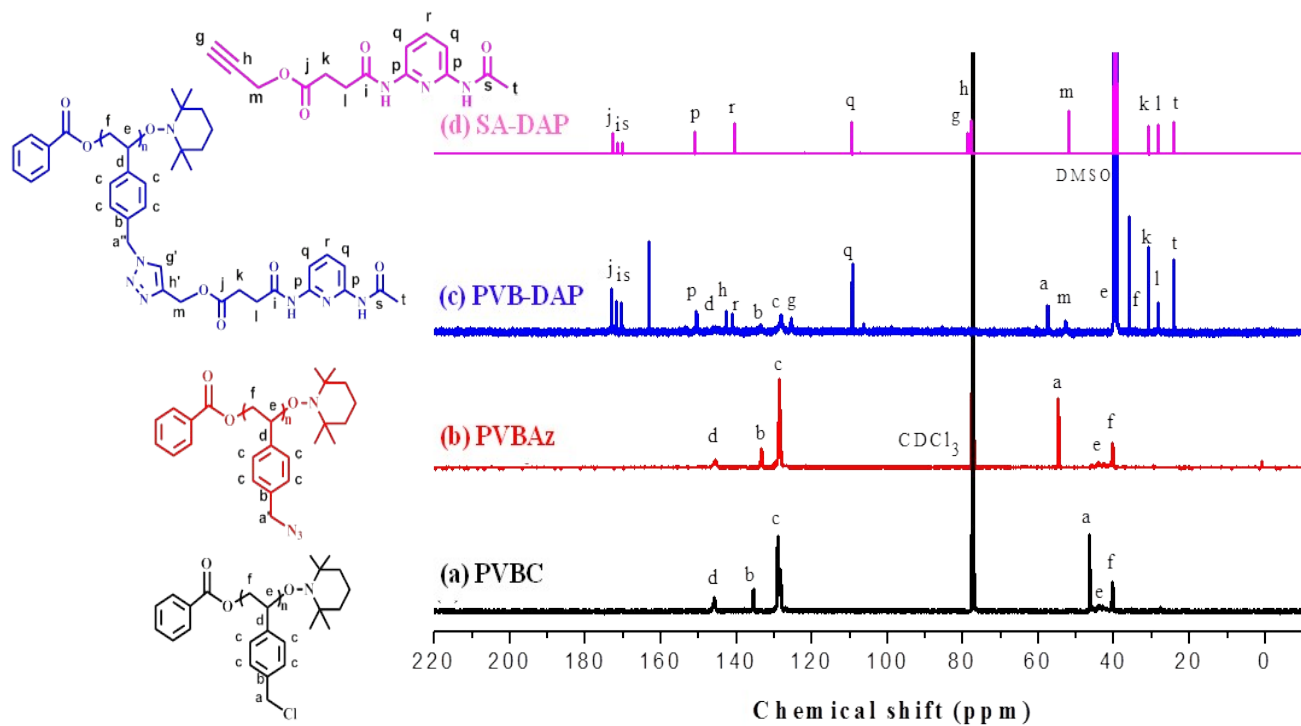


Fig. S1: ^{13}C NMR spectra of (a) PVBC and (b) PVBAz in CDCl_3 and of (c) PVB-DAP and (d) SA-DAP in $\text{DMSO}-d_6$.

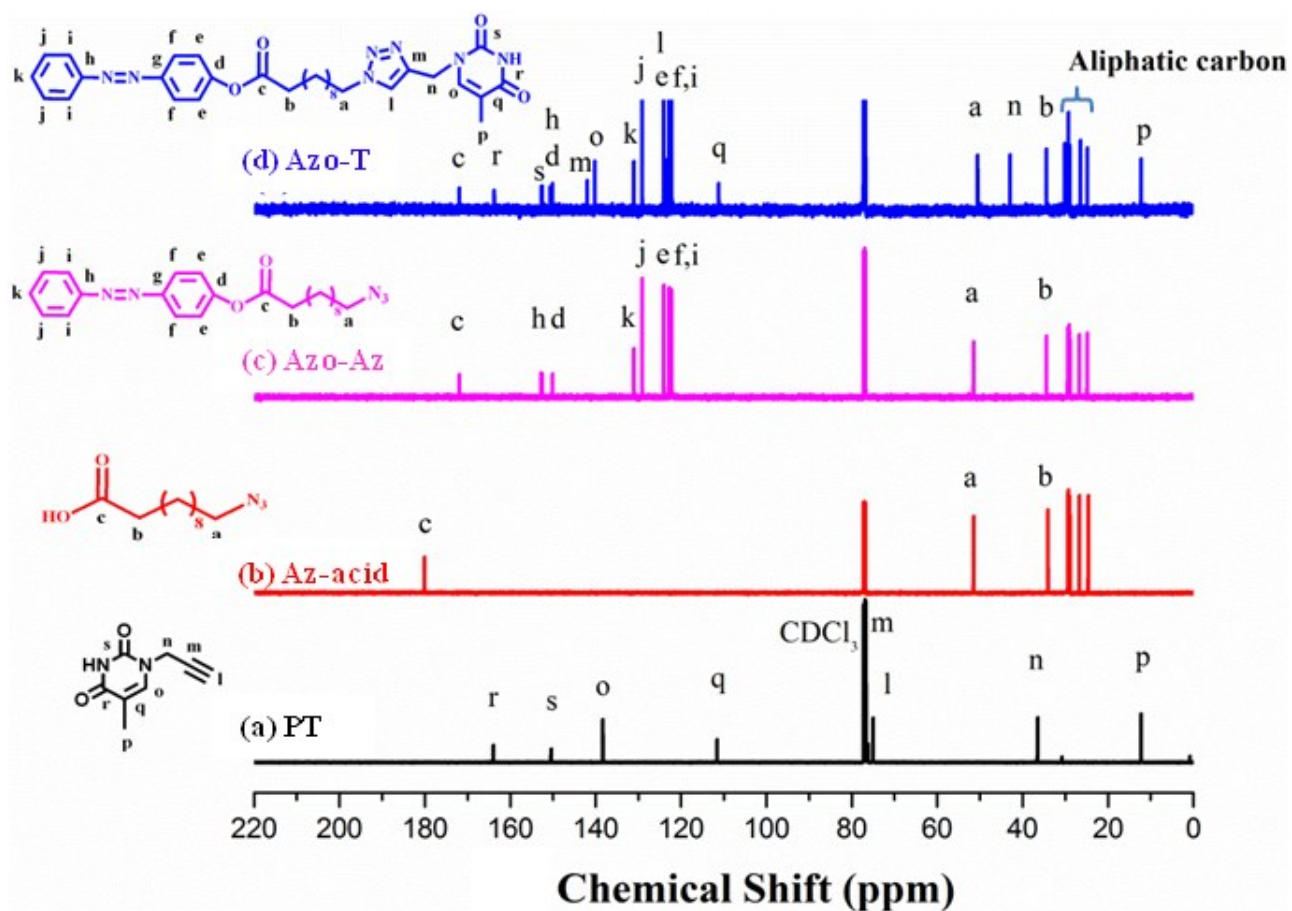


Fig. S2: ^{13}C NMR spectra of (a) PT and (b) Az-acid and of (c) Azo-Az and (d) Azo-T in CDCl_3 .

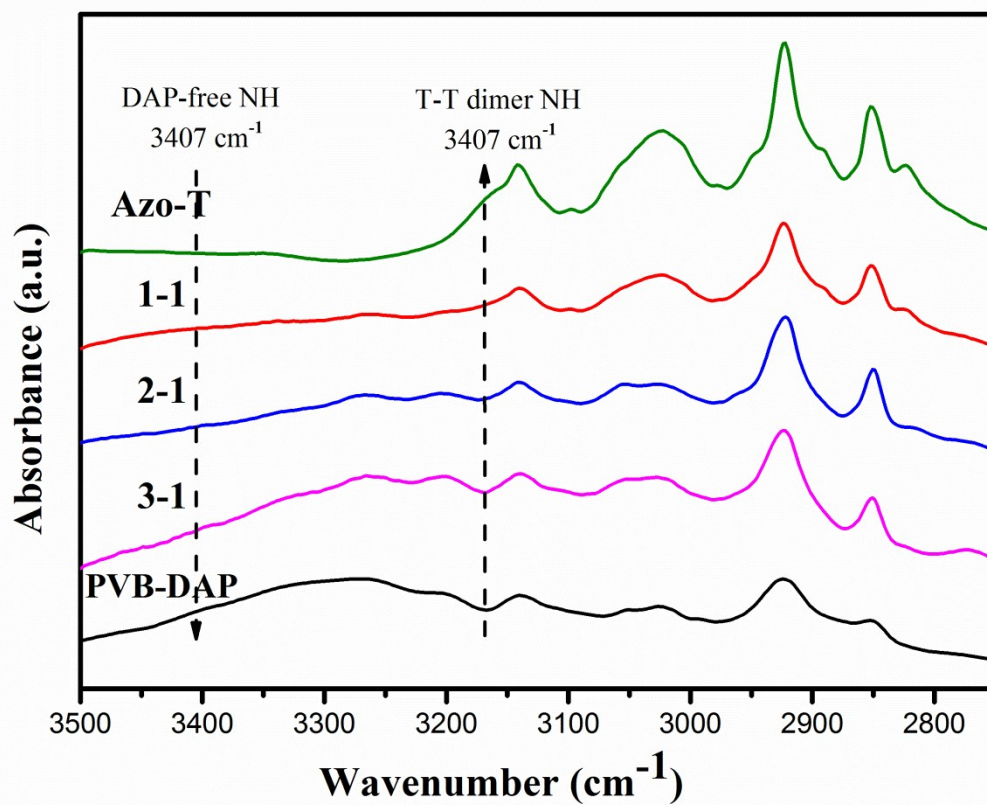


Fig. S3: FTIR spectrum of the PVB-DAP/Azo-T blend system in the range 2750–3500 cm^{-1} .

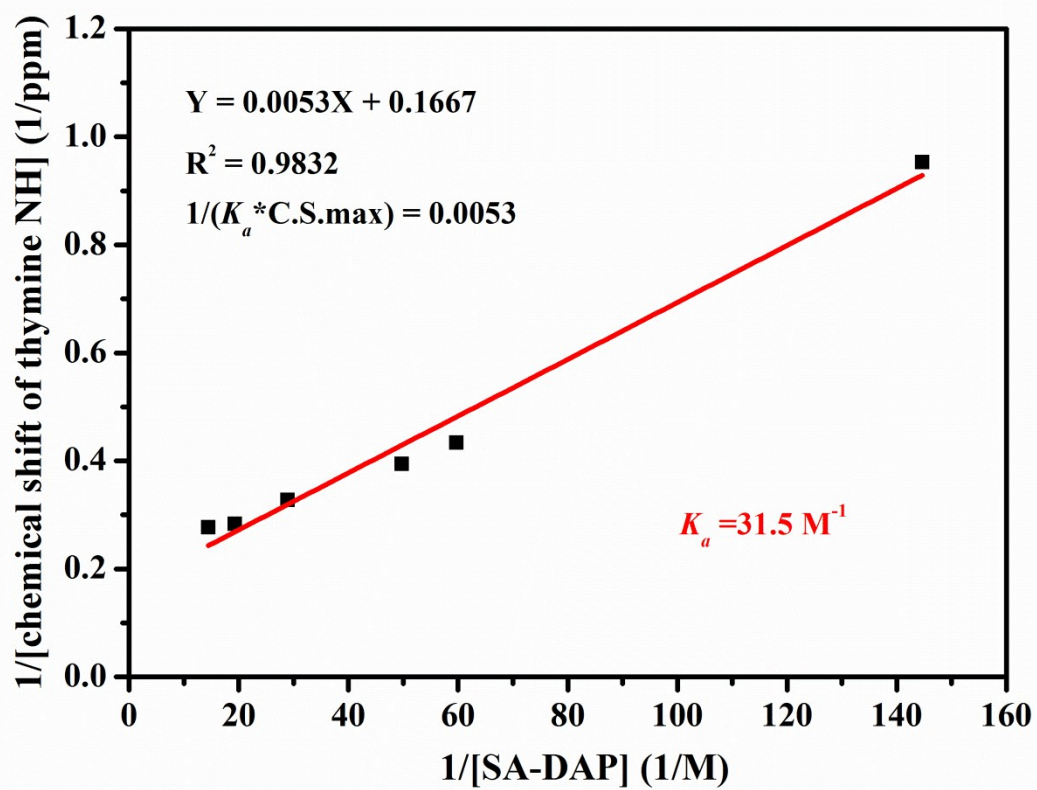


Fig. S4: Benesi-Hildebrand plots for calculation of the association constant of Azo-T/SA-DAP in 1,1,2,2-tetrachloroethane- d_2 at 25 °C.

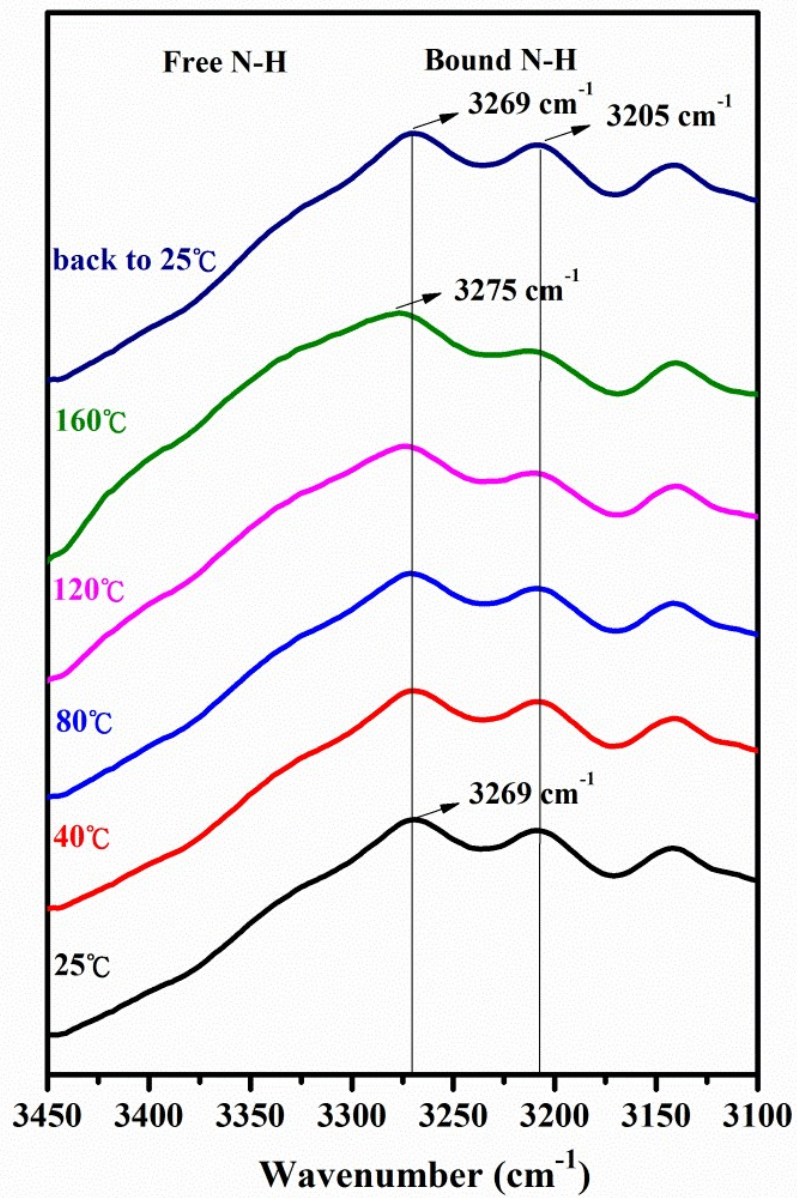


Fig. S5: Variable-temperature FTIR spectra of the PVB-DAP/Azo-T (2/1) blend system.

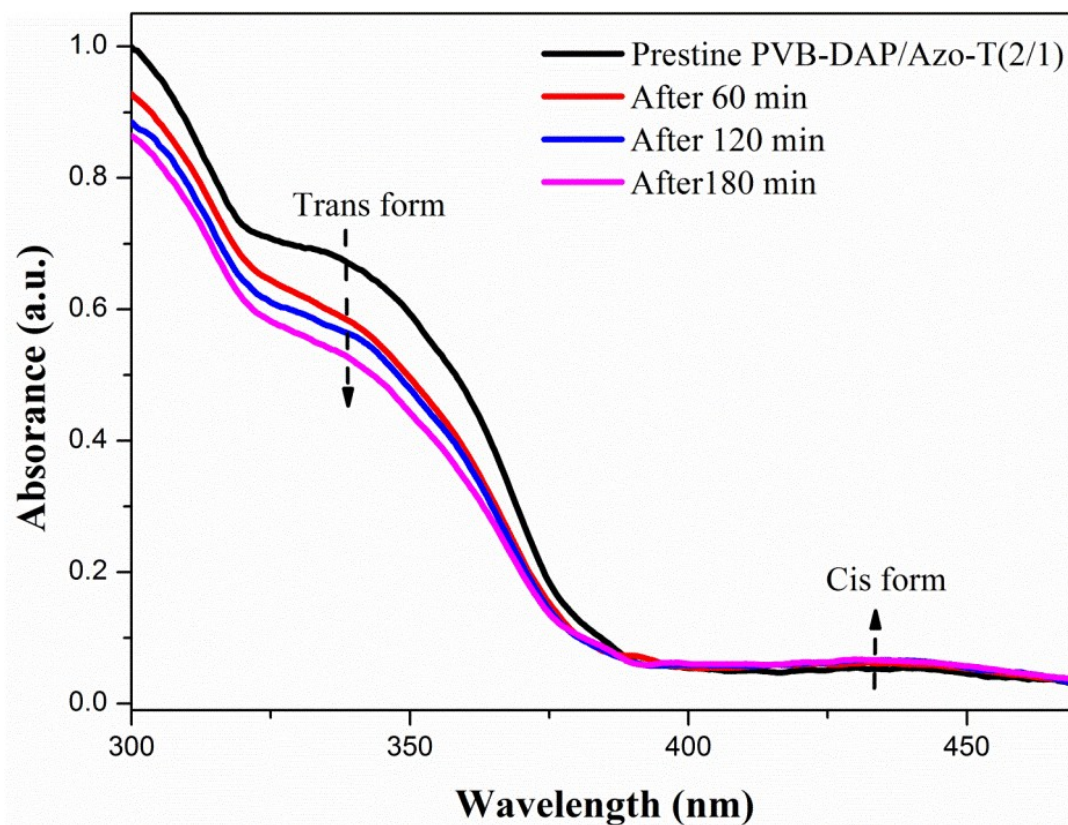


Fig. S6: UV-Vis spectra of the supramolecular complex PVB-DAP/Azo-T (2/1) blend thin film illumination under 365 nm UV for different time.

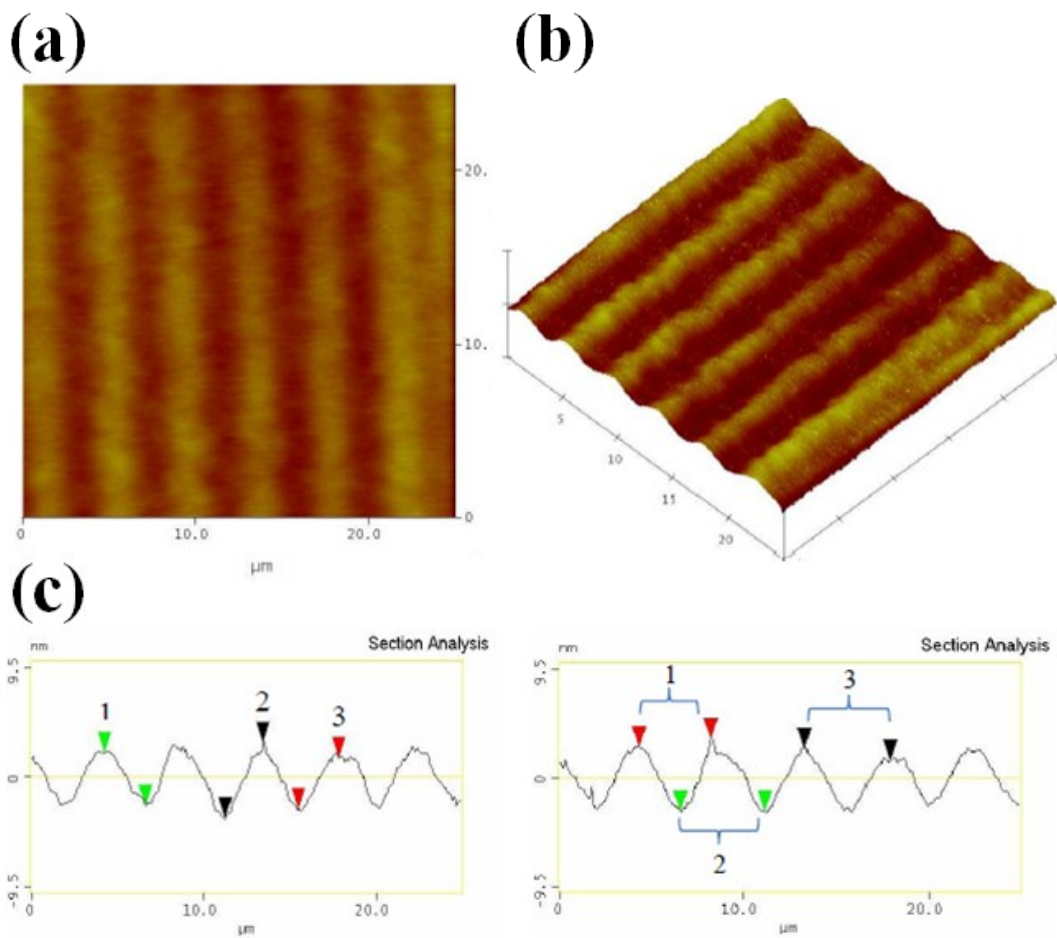


Fig. S7: AFM images of surface relief structures: (a) flattened image, (b) 3D image, and (c) section analysis for calculation of the thickness.

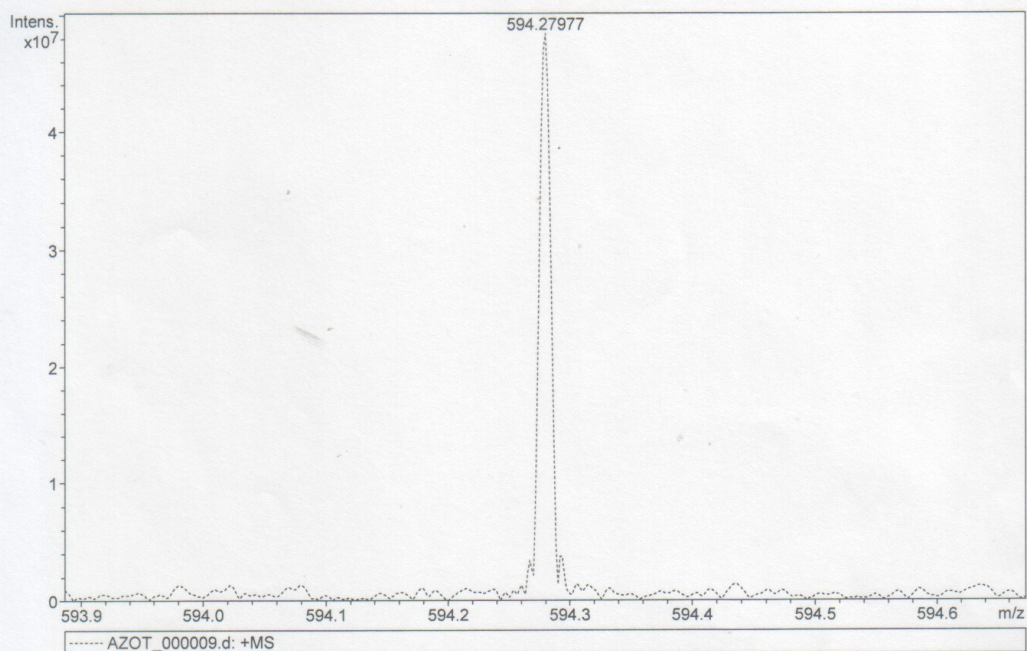
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\c7\AZOT_000009.d
Method broadband first signal
Sample Name Azo-T
Comment ESI Positive

7/16/2015 1:14:03 PM

Instrument: FT-MS solariX



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
594.27977	1	C 31 H 37 N 7 Na O 4	100.00	594.27992	0.15	0.26	46.2	16.5	even	ok

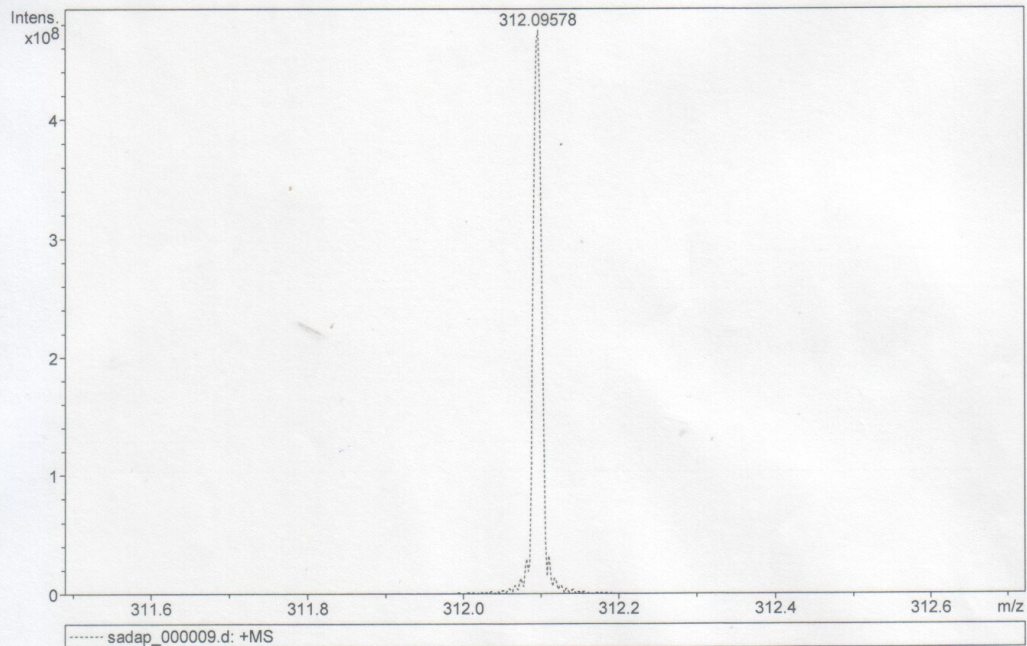
Fig. S8: ESI mass spectrum of Azo-T.

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\c7\sadap_000009.d
Method broadband first signal
Sample Name SA-DAP
Comment ESI Positive

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Instrument: FT-MS solariX



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
312.09578	1	C 14 H 15 N 3 Na O 4	100.00	312.09548	-0.30	-0.97	3.3	8.5	even	ok

Fig. S9: ESI mass spectrum of SA-DAP.