Electronic Supplementary Information

for

Electrospun nanofiber and multi-responsive supramolecular assemblies constructed by a pillar[5]arene-based receptor**

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1. Materials and Methods

Starting materials and reagents were purchased from Aldrich, Aladdin and Gibco, and used as received. All reagents were purchased from commercial sources and used without further purification, unless otherwise noted. The products were purified by column chromatography over silica gel. $^1$H-NMR and $^{13}$C-NMR spectra were recorded at 25 ºC on a Bruker AVANCE III 300 and 500 MHz and 125 MHz, respectively, and TMS was used as internal standard. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvent (CDCl$_3$: 7.260 ppm), and coupling constants were recorded in Hertz (Hz). Mass spectra were recorded on Bruker Daltonics Autoflex Speed Series: High-Performance MALDI-TOF Systems. Viscosity measurements were carried out with Ubbelohde micro viscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 298K in chloroform. The two-dimensional diffusion-ordered NMR spectra were recorded on a Bruker AVANCE III 600 MHz. Scanning electron microscopy (SEM) investigations were collected on a JEOL JSM6700F. Transmission electron microscopy (TEM) images were collected on a JEM-2100F instrument at an accelerating voltage of 120 KV. Atomic force microscopy (AFM) was carried out in the tapping mode with a Nanoscope IIIa scanning probe microscope from Digital Instruments under ambient conditions. Electrospun supramolecular polymer nanofibers were obtained from monomer 1 (300 mM in chloroform) by using electrospinning setup consisted of a plastic syringe positioned vertically with metallic nozzle at high electric potential pointing downwards and a grounded aluminum foil static collector. The vertical distance between the nozzle and the collector was about 24 cm. The electrospinning solution was loaded into a 5 mL plastic syringe with nozzle diameters of $\Phi_{\text{inner}} = 0.84$ mm and $\Phi_{\text{outer}} = 1.27$ mm. The voltage was set at 20-25 kV supplied by a high voltage power unit (ES60P-20W/DDPM, Gamma, USA).
2 General Procedure for the Synthesis of Monomer 1

![Synthetic route to monomer 1](image)

**Scheme S1** Synthetic route to monomer 1.


Copillar[5]arene 4\textsuperscript{S1} was synthesized according to our previous report.

White solid, m.p. 178-179 °C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta = 6.81-6.75 \text{ (m, 9H)}, 6.69 \text{ (s, 1H)}, 3.78 \text{ (s, 10H)}, 3.67-3.61 \text{ (m, 29H)}, 3.01 \text{ (s, 2H)}, 1.63 \text{ (s, 4H)}. \)
Figure S1. $^1$H NMR spectrum (CDCl$_3$, 298 K, 300 MHz) of 4.


Copillar[5]arene 4 (2.61 g, 3 mmol), sodium azide (0.39 g, 6 mmol) and DMF (25 mL) were added into a 50 mL round-bottom flask. After stirring at 80 °C for 10 h, the mixture was cooled to room temperature and poured into water (100 mL). The precipitate was collected by filtration, and washed with water to yield 5 as a white solid (2.25 g, 90%). $^1$H NMR (300 MHz, CDCl$_3$, 298 K) δ (ppm): 6.81−6.75 (m, 9H), 6.70 (s, 1H), 3.82−3.67 (m, 12H), 3.65−3.63 (m, 27H), 3.01−2.94 (m, 2H), 1.66−1.62 (m, 2H), 1.47−1.43 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$, 298 K) δ (ppm): 150.86, 150.80, 150.77, 150.75, 150.73, 150.72, 150.70, 149.90, 128.57, 128.36, 128.30, 128.25, 128.18, 114.08, 114.03, 114.01, 113.98, 113.93, 113.80, 67.80, 55.78, 55.71,
50.88, 29.78, 29.71, 29.66, 29.60, 29.55, 29.47, 26.89, 26.85, 25.26. MS (MALDI–TOF): calcd for C_{48}H_{55}O_{10}N_{3}, \text{m/z} = 834.3705 [M]^+, found \text{m/z} = 834.3726 (100.0%), 835.3736 (53.7%), 836.2736 (16.7%), 837.2739 (3.7%).

**Figure S2.** $^1$H NMR spectrum (300 MHz, CDCl$_3$, 298 K) of 5.

**Figure S3.** $^{13}$C NMR spectrum (125 MHz, CDCl$_3$, 298 K) of 5.
2.3 Synthesis of compound 3.

\[
\begin{align*}
\text{HO} & \quad \text{OH} \\
\text{7} & \quad + \quad \text{Br} \\
\text{NaH} & \quad \text{DMF} \\
\text{8} & \quad (60\%)
\end{align*}
\]

Sodium hydride (w/w = 60%, 0.48 g, 12 mmol) was slowly added to a solution of 7 (3.5 g, 20 mmol) in anhydrous DMF (25 mL) at 0 °C under nitrogen. The mixture was stirred at 0 °C for 0.5 h under nitrogen. Propargyl bromide (0.891 mL, 10 mmol) was injected slowly to the reaction flask. The mixture was stirred at 25 °C for 24 h. While the solution turned brown, the mixture was filtered off. The collected filtrate was diluted by CH₂Cl₂ (50 mL) and further washed with H₂O three times. The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatograph (EtOAc / petroleum ether 1:4) to afford desired product 8 as slightly yellowish oil (1.28 g, 60%). ¹H NMR (300 MHz, CDCl₃, 298 K) δ (ppm): 4.11 (d, \( J = 2.4 \) Hz, 2H), 3.61 (t, \( J = 6.6 \) Hz, 2H), 3.49 (t, \( J = 6.6 \) Hz, 2H), 2.40 (t, \( J = 2.4 \) Hz, 1H), 1.59–1.52 (m, 4H), 1.45 (br, 1H), 1.35–1.24 (m, 12H).
8 (2.12 g, 10 mmol) was added in a well-dried flask containing anhydrous dichloromethane (40 mL) under a nitrogen atmosphere, then triphenylphosphine (3.15 g, 12 mmol) was added to this solution. After the reaction mixture was cooled to 0 °C, carbon tetrabromide (3.98 g, 12 mmol) in CH₂Cl₂ (20 mL) was added dropwise. After stirring overnight, the solvent from the reaction mixture was evaporated out. Diethyl ether (13 mL) was added to the reaction mixture, kept for 5 minutes and filtered. The same process (addition of ether, filtration) was repeated thrice. The residue was subjected to flash column chromatography to obtain the final product (2.1 g, 75%). $^1$H NMR (300 MHz, CDCl₃, 298 K) δ (ppm): 4.13 (d, $J = 2.4$ Hz, 2H), 3.48 (t, $J = 6.6$ Hz, 2H), 3.40 (t, $J = 6.9$ Hz, 2H), 2.41 (t, $J = 2.4$ Hz, 1H), 1.85–1.80 (m, 2H), 1.61–1.54 (m, 2H), 1.42–1.28 (m, 12H). MS (EI): m/z 274.8 (100.0%), 276.8 (83.3%), 275.8 (14.1%), 277.8 (13.7%).

Figure S5. $^1$H NMR spectrum (300 MHz, CDCl₃, 298 K) of 8.  

8
Figure S6. $^1$H NMR spectrum (CDCl$_3$, 298 K, 300 MHz) of 6.$^2$

Figure S7. EI-MS of 6.
To a stirred mixture of 5 (0.834 g, 1 mmol), 6 (0.33 g, 1.2 mmol) and CuI (19 mg, 0.1 mmol) in CHCl₃ (10 mL) was added 2,6-lutidine (0.117 mL, 1 mmol) at room temperature. After stirring for 15 h at room temperature, the reaction mixture was diluted with CH₂Cl₂ (20 mL) and then with aqueous NH₄Cl solution (30 mL). The mixture was stirred for an additional 15 minutes and two layers were separated. The aqueous layer was extracted with CH₂Cl₂ (3 mL × 3) and the combined organic layers were dried over anhydrous Na₂SO₄, concentrated in vacuo. The crude residue was purified by flash column chromatography (EtOAc / petroleum ether, 1:2) to give the desired product 3 as a white solid (0.9 g, 81%).

¹H NMR (500 MHz, CDCl₃, 298 K) δ (ppm): 7.53 (s, 1H), 6.90-6.78 (m, 9H), 6.71 (s, 1H), 4.67 (s, 2H), 4.45 (t, J = 6.6 Hz, 2H), 3.77-3.63 (m, 39H), 3.47 (s, 2H), 2.15 (t, J = 7.5 Hz), 1.52 (s, 2H), 1.23 (s, 4H), 1.05 (s, 4H), 0.60 (s, 2H), -0.11 (s, 2H), -0.51 (s, 1H), -0.76 (s, 1H).

¹³C NMR (125 MHz, CDCl₃, 298 K) δ (ppm): 150.75, 150.45, 150.42, 150.37, 150.28, 150.23, 149.42, 148.85, 128.21, 128.01. 127.77, 122.42, 114.98, 113.49, 113.31, 113.23, 113.16, 69.78, 67.65, 64.25, 64.18, 60.40, 55.58, 55.38, 53.60, 46.25, 29.99, 29.72, 29.58, 29.33, 29.26, 29.13, 28.42, 27.73, 27.51, 27.06, 26.28. MS (MALDI–TOF) calcd for C₆₁H₇₈O₁₁N₃Br, m/z = 1129.5049 [M + H₂O], found m/z =1129.5697 (100.0%), 1130.5726 (61.3%), 1131.5916 (12.4%).
Figure S8. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 298 K) of 3.

Figure S9. $^{13}$C NMR spectrum (125 MHz, CDCl$_3$, 298 K) of 3.
2.4 Synthesis of compound 2.

*N,N*-dimethylamine (2 equiv.) and potassium hydroxide (0.12 g, 2 equiv.) were added to a solution of compound 3 (1.1 g, 1 mmol) in DMF (10 mL). Then, the reaction mixture was stirred at 50 °C for 5h, cooled to room temperature and added to CH₂Cl₂ (30 mL). The solution was washed with H₂O three times. The organic layer was removed under vacuum and purified by column chromatography (DCM / EtOAc, 20:1) to afford compound 2 as a yellowish liquid. ¹H NMR (500 MHz, CDCl₃, 298 K) δ (ppm): 7.45 (s, 1H), 6.80-6.73 (m, 9H), 6.66 (s, 1H), 4.59 (s, 2H), 4.28 (s, 2H), 3.75-3.44 (m, 39H), 2.23-2.20 (m, 8H), 2.00 (s, 2H), 1.72 (s, 2H), 1.50 (s, 2H), 1.42 (s, 2H), 1.26-1.02 (m, 12H). ¹³C NMR (125 MHz, CDCl₃, 298 K) δ (ppm): 150.7, 149.7, 145.6, 128.3, 128.2, 122.1, 115.0, 114.0, 70.9, 67.3, 64.4, 60.4, 59.9, 55.8, 55.7, 53.1, 49.8, 46.2, 45.5, 36.3, 29.6, 29.5, 29.4, 27.7, 27.5, 27.1, 26.7, 26.0, 21.0. MS (MALDI–TOF) calcd for C₆₃H₄₅O₁₁N₄, m/z = 1073.3614 [M]⁺, found m/z =1073.3594.
**Figure S11.** $^1$H NMR spectrum (500 MHz, CDCl$_3$, 298 K) of 2.

**Figure S12.** $^{13}$C NMR spectrum (125 MHz, CDCl$_3$, 298 K) of 2.
2.5 Synthesis of monomer 1.

To the solution of 2 (0.536 g, 0.5 mmol) in DCM / MeOH (5 mL) was added HCl aqueous to adjust pH < 2, then a saturated aqueous solution of NH₄PF₆ (5 equiv.) was added to the mixture. The resulting solution was stirred at room temperature for 2 hours. The solvent was removed in vacuo, the residue was suspended in water (10 mL). The precipitate was filtered off and washed with deionized water to afford targeted compound 1 as a white solid (0.424 g, 75 %). ¹H NMR (500 MHz, CDCl₃, 298 K) δ (ppm): 7.68 (s, 1H), 6.88-6.84 (m, 9H), 6.81 (s, 1H), 4.65 (s, 2H), 4.51 (t, J = 5.5 Hz, 2H), 3.78-3.55 (m, 41H), 2.21 (s, 2H), 1.81 (s, 2H), 1.60 (s, 8H), 1.25 (s,
4H), 1.22 (s, 4H), 1.03 (s, 2H), 0.59 (s, 2H), -0.27 (s, 2H), -1.23 (s, 2H). $^{13}$C NMR
(125 MHz, CDCl$_3$, 298 K) δ (ppm): 150.7, 150.5, 149.7, 145.4, 128.9, 128.8(5),
128.8(0), 123.1, 115.1, 114.2, 114.1(9), 114.1(5), 114.0, 113.8, 68.3, 64.0, 56.2, 50.1,
42.9, 30.3, 30.1, 29.4, 29.3, 29.2, 29.1, 29.0, 27.4, 26.9(5), 26.2, 25.7, 23.4. MS
(MALDI–TOF) calcd for C$_{63}$H$_{85}$O$_{11}$N$_4$, m/z = 1074.3694 [M-PF$_6$]$^+$, found m/z
=1074.3608.

Figure S14. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 298 K) of 1.
Figure S15. $^{13}$C NMR spectrum (125 MHz, CDCl$_3$, 298 K) of 1.

Figure S16. MS (MALDI-TOF) of 1.
3 Self-Aggregation Behavior of Monomer 1 at Low Concentration

Monomer-aggregate equilibrium equation in solution:

\[ n \text{ Monomer} \xleftrightarrow{K_{agg}} \text{ aggregate} \]

\[ \frac{C_{\text{mon}}}{C_{\text{tot}} + nC_{\text{agg}}} = 1 \]

\[ C_{\text{tot}} = C_{\text{mon}} + nC_{\text{agg}} \]

\[ \delta_{\text{obs}} = N_{\text{mon}}\delta_{\text{mon}} + N_{\text{agg}}\delta_{\text{agg}} \]

\[ \delta_{\text{obs}} = C_{\text{tot}}\frac{\delta_{\text{mon}} + nC_{\text{agg}}\delta_{\text{agg}}}{C_{\text{tot}} + nC_{\text{agg}}} \]

\[ (1 - \frac{nC_{\text{agg}}}{C_{\text{tot}}})\delta_{\text{mon}} + \frac{nC_{\text{agg}}}{C_{\text{tot}}}\delta_{\text{agg}} \]

\[ \Rightarrow \delta_{\text{obs}} - \delta_{\text{mon}} = \frac{nC_{\text{agg}}}{C_{\text{tot}}} (\delta_{\text{agg}} - \delta_{\text{mon}}) \]

\[ \Rightarrow C_{\text{agg}} = \frac{\delta_{\text{obs}} - \delta_{\text{mon}}}{\delta_{\text{agg}} - \delta_{\text{mon}}} \cdot \frac{C_{\text{tot}}}{n} \]

\[ K_{agg} = \frac{C_{\text{agg}}}{(C_{\text{tot}} - nC_{\text{agg}})^n} \]

\[ \Rightarrow \ln K_{agg} = \ln C_{\text{agg}} - n \ln(C_{\text{tot}} - nC_{\text{agg}}) \]

\[ = \ln \frac{\delta_{\text{obs}} - \delta_{\text{mon}}}{\delta_{\text{agg}} - \delta_{\text{mon}}} \cdot \frac{C_{\text{tot}}}{n} - n \ln(C_{\text{tot}} - n\delta_{\text{obs}} - \delta_{\text{mon}} \cdot \frac{C_{\text{tot}}}{n}) \]

\[ = \ln \frac{\delta_{\text{obs}} - \delta_{\text{mon}}}{\delta_{\text{agg}} - \delta_{\text{mon}}} \cdot \frac{C_{\text{tot}}}{n} - n \ln \frac{\delta_{\text{agg}} - \delta_{\text{obs}}}{\delta_{\text{agg}} - \delta_{\text{mon}}} \cdot C_{\text{tot}} \]

\[ = \ln \frac{\delta_{\text{obs}} - \delta_{\text{mon}}}{\delta_{\text{agg}} - \delta_{\text{mon}}} \cdot C_{\text{tot}} - n \ln \frac{\delta_{\text{agg}} - \delta_{\text{obs}}}{\delta_{\text{agg}} - \delta_{\text{mon}}} \cdot C_{\text{tot}} \]

\[ \Rightarrow \ln K_{agg} + \ln n = \ln(\delta_{\text{mon}} - \delta_{\text{agg}})C_{\text{tot}} - \ln(\delta_{\text{mon}} - \delta_{\text{agg}})C_{\text{tot}} - n \ln(\delta_{\text{obs}} - \delta_{\text{agg}})C_{\text{tot}} + n \ln(\delta_{\text{mon}} - \delta_{\text{agg}}) \]

\[ \Rightarrow \ln(\delta_{\text{mon}} - \delta_{\text{agg}})C_{\text{tot}} = n \ln(\delta_{\text{obs}} - \delta_{\text{agg}})C_{\text{tot}} + \ln K_{agg} + \ln n - (n - 1) \ln(\delta_{\text{obs}} - \delta_{\text{agg}}) \quad (I) \]

Substitute \( n = 2 \) in the monomer-aggregate equation gives the monomer-dimer equilibrium equation as follow:

\[ \delta_{\text{obs}} = \delta_{\text{dimer}} + \{(\delta_{\text{mon}} - \delta_{\text{dimer}})^{-1} + (1 + 8 K_{\text{dimer}}C_{\text{tot}})^{1/2}\}^2/(4 K_{\text{dimer}}C_{\text{tot}}) \quad (II) \]
Figure S17. $^1$H NMR (500 MHz, CDCl$_3$, 298 K) spectra of monomer 1 at low concentrations (the concentration refers to the total concentration of initial monomer 1). From up to bottom: (a) 0.10 mM, (b) 0.21 mM, (c) 0.40 mM, (d) 0.61 mM, (e) 1.01 mM, and (f) 1.21 mM.
Figure S18. Plot of chemical shift ($\delta_{\text{obs}}$) vs. the total concentration ($C_{\text{tot}}$) of monomer 1 for $\delta_{\text{mon}}$. The chemical shift that is plotted here ($\delta_{\text{obs}}$) is that data shown in Figure S17. Dots are experimental data and the curve is obtained through non-linear fitting of data to equation (II).

Figure S19. Plot of chemical shift ($\delta_{\text{obs}}$) vs the reciprocal of the total concentration ($C_{\text{tot}}$) of monomer 1 for $\delta_{\text{agg}}$. Dots are experimental data and the curve is best fit. The value 0.948 was obtained from equation (II) through non-linear fitting based on the data in Figure S17.
Figure S20. Plots from $^1$H NMR data of monomer 1 as a function of total concentration to determine the aggregation equilibrium constant and aggregation number. Plots of $\ln[C_{\text{tot}} (\delta_{\text{mon}} - \delta_{\text{obs}})]$ vs. $\ln[C_{\text{tot}} (\delta_{\text{obs}} - \delta_{\text{agg}})]$ give a straight line, from which the slope and the intercept can be calculated to yield $n$ and $K_{\text{agg}}$ according to equation (I).

According to equation (I), aggregation number $n$ and self-aggregation constant $K_{\text{agg}}$ can be obtained, where $C_{\text{tot}}$ refers to the total concentration of initial monomer 1, $\delta_{\text{mon}}$ and $\delta_{\text{agg}}$ refers the extrapolated values of the monomer and aggregate, respectively. By plotting $\delta_{\text{obs}}$ against the total concentration and extrapolating to zero monomer concentration, the chemical shift of the monomer ($\delta_{\text{mon}}$) can be estimated graphically from equation (II) (Fig. S17 and S18). Extrapolation of the concentration to infinity yields the chemical shift of the aggregate ($\delta_{\text{agg}}$) (Fig. S19). Plots of $\ln[C_{\text{tot}} (\delta_{\text{mon}} - \delta_{\text{obs}})]$ vs. $\ln[C_{\text{tot}} (\delta_{\text{obs}} - \delta_{\text{agg}})]$ give a straight line, from which the slope and the intercept can be calculated to yield $n$ and $K_{\text{agg}}$ according to equation (I) (Fig. S20).
Figure S21. Partial variable temperature $^1$H NMR spectra (500 MHz, 1.0 mM, CDCl$_3$) of monomer 1.
4. Self-Assembly Behavior of monomer 1

![NMR spectra](image)

**Figure S22.** $^1$H NMR spectra of monomer 1 (500 MHz, CDCl$_3$, 298K) at different concentrations. From bottom to up: (a) 1.5 mM; (b) 20 mM; (c) 58 mM; (d) 75 mM; (e) 100 mM; (f) 120 mM; (g) 150 mM; (h) 200 mM; (i) 250 mM.

The concentration-dependent $^1$H NMR spectra of monomer 1 spanning a range of concentrations from 1.5 mM to 250 mM were carried out, providing important insights into its self-assembly behaviour at high concentrations in solution. With increasing concentration of initial monomer 1, its concentration-dependent $^1$H NMR spectra became complicated, whereas the proton signals $H^2$ of triazole moiety shifted downfield constantly. At a monomer concentration of 250 mM, the initially split peaks disappeared along with the broadening of all signals, manifesting the monomer 1 self-assembled into high molecular weight assemblies.
5. 2D ROESY Spectroscopy of Monomer 1 and Monomer 2

Figure S23. (a) 2D ROESY spectroscopy of monomer 1 at a concentration of 35 mM;
(b) Partial 2D REOSY spectroscopy of monomer 1 (600 MHz, CDCl₃, 298 K).
The ROESY spectroscopy of 1 exhibited clear cross-peaks (A and B) between tertiary ammonium alkyl chain (H⁷, H⁸, H⁹ and H¹⁰) and pillar[5]arene moiety, demonstrating that the tertiary ammonium alkyl chain was deeply threaded into the cavity of pillar[5]arene moiety (Fig. S23). In order to compare the binding strength, monomer 2 was chosen to run ROESY experiment (Fig. S24a and S24b). Highly different from the tertiary ammonium-version of side alkyl chain, few cross-peaks were observed between tertiary amine alkyl chain and pillar[5]arene moiety, suggesting the very weak non-covalent interactions between the pillar[5]arene and tertiary amine alkyl side chains moieties of 2.
Figure S24. (a) 2D ROESY spectroscopy of monomer 2 at a concentration of 35 mM;
(b) Partial 2D REOSY spectroscopy of monomer 2 (600 MHz, CDCl$_3$, 298 K).
6. 2D Diffusion-Ordered NMR Spectroscopy

Figure S25. 2D diffusion-ordered NMR spectroscopy (600 MHz, 298 K): (●) multiple concentrations in CDCl₃. (♦) 160 mM monomer 1 in the presence of 1.5 equiv. of Et₃N in CDCl₃. (■) 160 mM monomer 1 in the presence of 1.2 equiv. of TBACl in CDCl₃. (▼) 160 mM monomer 1 in acetone-d₆ (the diffusion coefficient has been converted according to Stokes-Einstein equation).

Measurements of diffusion coefficients (D) were performed on monomer 1 from 0.1 to 160 mM in CDCl₃ (blue dots). As the monomer concentration increased from 0.1 to 160 mM, the weight-average diffusion coefficients decreased from 9.46 × 10⁻¹⁰ to 1 × 10⁻¹⁰ m²s⁻¹, signifying the concentration-dependence of the linear supramolecular polymerization of 1. A plot of D values against concentration revealed a sharp decrease in D between 0.1 to 50 mM with comparatively little further change in D from 50 to 160 mM. This large decrease in D over a small change in concentration corroborated the formation of linear supramolecular polymers.
7. Specific Viscosity of Monomer 1 in Chloroform

Figure S26. Specific viscosity of monomer 1 \textit{versus} the monomer concentration (in chloroform, 298 K).

The linear supramolecular polymer assembled from monomer 1 exhibited a distinct viscosity transition, and was characterized by a change in slope in the double logarithmic plots of specific viscosity \textit{versus} the monomer concentration. At low concentration, the slope of the curve was 1.13, demonstrating a linear relationship between specific viscosity and monomer concentration, which was characteristic for non-interacting assemblies of constant size; these results indicated the presence of dimer or cyclic oligomer in diluted solutions. When concentration exceeded the critical polymerization concentration (CPC, approximately 59.6 mM), a sharp increase in the viscosity was observed (slope = 2.49). This strong concentration-dependence manifested the formation of linear supramolecular polymers with increasing size.
8. SEM, TEM and AFM Images of Supramolecular Polymer Based on Monomer 1 by Electrospinning

SEM:

TEM:
AFM:

h)

i)

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Figure S27. (a-d) SEM images of supramolecular polymer nanofibers; (e-g) TEM images of the supramolecular polymer nanofibers; (h and i) AFM images and section analysis of supramolecular polymer nanofibers

9. Reversible Stimuli-Responsive Disassembly-Reassembly Transition of the Supramolecular Polymer

Scheme S2 Representation of stimuli-responsive behaviours of the supramolecular polymer from monomer 1. The external stimuli include pH, counter anion and solvent composition.
9.1 pH-responsive NMR experiments.

X = CF₃COO or PF₆

**Figure S28.** Partial ^1^H NMR spectra (500 MHz, 298 K, CDCl₃) of (a) monomer 1 (60 mM), (b) monomer 1 (60 mM) after the addition of 1.5 equiv. of Et₃N, (c) monomer 1 (60 mM) after the addition of 1.5 equiv. of Et₃N and then 2.0 equiv. of TFA.
9.2 Counter anion-responsive NMR experiments.

* indicates (CH$_3$CH$_2$CH$_2$CH$_2$)$_4$N$^+$ X$^-$ (X = Cl or PF$_6$)

**Figure S29.** Partial $^1$H NMR spectra (500 MHz, 298 K, CDCl$_3$) of (a) monomer 1 (60 mM), (b) monomer 1 (60 mM) after the addition of 1.2 equiv. of TBACl, (c) monomer 1 (60 mM) after the addition of 1.2 equiv. of TBACl and then 1.5 equiv. of AgOTf, the broadening peaks (brown region) are ascribed to coordination between triazole and excessive Ag$^+$. 

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9.3 Solvent composition-responsive NMR experiments.

\( \chi \) indicates the volume fraction of acetone in the mixed solvent system.

* indicates acetone-\( d_6 \).

Figure S30. Partial \( ^1H \) NMR spectra of monomer 1 (60 mM) in mixed solvents (500 MHz, 298 K): a) monomer 1 in CDCl\(_3\); b) 1 in 4 : 1 CDCl\(_3\) / acetone-\( d_6 \) (\( \chi = 0.2 \)); 1 in 1:1 CDCl\(_3\) / acetone-\( d_6 \) (\( \chi = 0.5 \)); 1 in 1 : 4 CDCl\(_3\)/acetone-\( d_6 \) (\( \chi = 0.8 \)); 1 in acetone-\( d_6 \) (\( \chi = 1 \)).
9.4 2D diffusion-ordered NMR experiments.

(a)

(b)
**Figure S31.** At a monomer 1 concentration of 160 mM, the diffusion coefficients (lg $D$) (600 MHz, 298 K): (a) in CDCl$_3$; (b) upon addition of 1.5 equivalent of Et$_3$N to a;
(c) upon addition of 1.2 equivalent of TBACl to a; (d) varying the fraction of acetone in the mixed solvent system ($\chi_{\text{acetone}} = 1$), the diffusion coefficient ($D$) was $3.362 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ according to Stokes-Einstein equation conversion.

These reversible assembly-disassembly transitions between supramolecular polymers and monomers were verified by means of 2D diffusion-ordered NMR spectroscopy analysis. At a monomer concentration of 160 mM, the diffusion coefficient ($D$) increased from $1 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ to $2.461 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, $2.845 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ and $3.362 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ respectively, along with the addition of Et$_3$N, TBACl or varying the fraction of acetone in the mixed solvent system ($\chi_{\text{acetone}} = 1$). These results demonstrated that decomplexation of supramolecular polymers occurred in response to the above external stimuli (as shown in Fig. S25, red, black, purple dots).

References

