

Supporting Information for

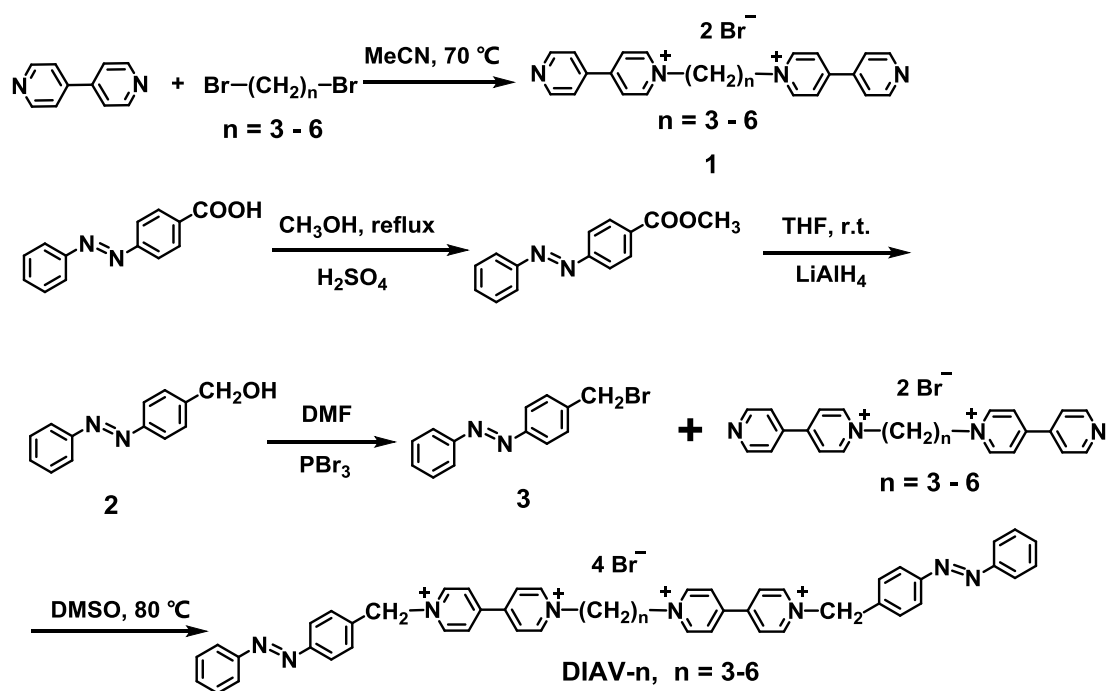
Controllable Supramolecular Polymerization through Host–Guest Interaction and Photochemistry

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1. Materials and methods

Materials were obtained from commercial suppliers, and were used directly without further purification. Asymmetric flow field flow fractionation (As4F) experiments were performed by Wyatt Technology Eclipse 3+ with multi-angle light scattering detector (Optilab rEX), Ultraviolet and Differential Refraction detector (DAWN HELEOS-II). UV-vis spectra were recorded by a HITACHI U-3010 spectrophotometer. ^1H NMR and DOSY spectra were recorded on a JOEL JNM ECA400 NMR Spectrometer (400 MHz). Spectra were recorded in deuterated acetic acid—sodium acetate buffer (50 mM, pH 4.75). Visible light was obtained with LED lamps with $\lambda \sim 420$ nm, UV light was obtained with a xenon lamp combined with band-pass filter (center wavelength ~ 365 nm).

2. Synthesis and characterization of DIAV-n monomers



Scheme S1. Synthesis route of DIAV-n monomers with different alkyl chain linkers.

Take the synthesis of DIAV-4 as a representative example, other DIAV-n monomers with different alkyl linkers follow the same procedure.

Compound 1 1,4-dibromobutane and 4,4'-bipyridine were heated in MeCN at 70 °C for 5 h. The solution was precipitated in diethyl ether, the precipitate was filtrated and dried in vacuum to obtain pale yellow product. ¹H NMR (400 MHz, DMSO-d₆, ppm): δ = 9.26 (d, 4H), 8.88 (d, 4H), 8.69 (d, 4H), 8.05 (d, 4H), 4.73 (m, 4H), 2.04 (m, 4H).

Compound 2 Azobenzene-4-carboxylic acid was refluxed in methonal catalyzed by concentrated H₂SO₄ for 5 h, and precipitated in water to obtain methyl azobenzene-4-carboxylate. Then methyl azobenzene-4-carboxylate was reduced by LiAlH₄ in THF at room temperature to obtain 4-(phenylazo)benzyl alcohol **2**. ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.93 (m, 4H), 7.52 (m, 4H), 4.80 (s, 2H).

Compound 3 Compound **2** was dissolved in DMF at -10 °C, and PBr₃ was gradually added in the solution. The mixture was stirred for 1 h, and precipitated in water. The product was purified by a flash chromatography (CH₂Cl₂ as eluent) to finally obtain a red powder **3**. ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.91 (m, 4H), 7.54 (m, 4H), 4.56 (s, 2H).

DIAV-4 Compound **3** and **1** were heated in DMSO at 80 °C for 12 h, the yielding yellow precipitate was filtrated and recrystallized in water to obtain a yellow powder DIAV-4 with full trans configuration. ¹H NMR (400 MHz, DMSO-d₆, ppm): δ = 9.55 (d, 4H), 9.41 (d, 4H), 8.79 (m, 8H), 7.96 – 7.79 (m, 12H), 7.58 (m, 6H), 6.05 (s, 4H), 4.75 (m, 4H), 2.06 (m, 4H). ESI-MS: [M-H]⁻ calcd 1077.05, found 1077.05.

Preparation of supramolecular polymers DIAV-n were dissolved in sodium acetate buffer (50 mM, pH = 4.75). Then a certain amount of CB[8] was added into the solution. The mixture was then heated at 80 °C, assisted by ultrasonic oscillation to obtain a homogeneous yellow solution, and finally cooled down to room temperature.

3. Comparison of supramolecular polymers formed by DIAV-n monomers with different alkyl linkers

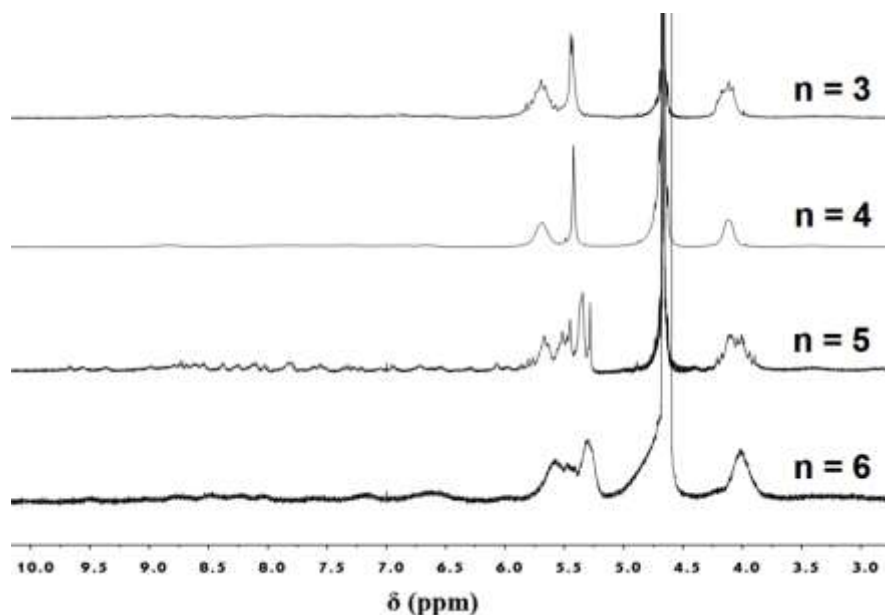


Figure S1. ^1H NMR spectra of supramolecular polymers formed by DIAV-n monomers with different alkyl chains.

To compare the ^1H NMR spectra of supramolecular polymers formed by different DIAV-n monomers with CB[8] in a molar ratio of 1:2, we found that both of samples from DIAV-3 and DIAV-4 showed broadened signals of DIAV and CB[8] molecules, while lots of multiple peaks from DIAV-5. The situation for DIAV-6 was something different. Owing to the poor solubility of this sample, the signal-noise ratio was very low, and the broaden effect of NMR peaks were mainly caused by the aggregation.

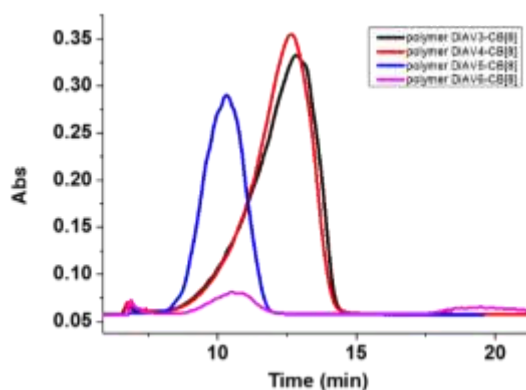


Figure S2. As4F elution curves of supramolecular polymers formed by DIAV-n monomers with different alkyl linkers. Elution solvent: HAc-NaAc buffer (50 mM, pH 4.75); concentration, $[\text{CB}[8]] = 1 \text{ mM}$; injection volume, 200 μL ; semipermeable membrane, PES 5kD.

As shown in Figure S2, As4F demonstrated relatively high molecular weights of supramolecular polymers formed by DIAV-3 and DIAV-4, and low molecular weights for DIAV-5 and DIAV-6.

4. Supplementary information for controllable supramolecular polymerization

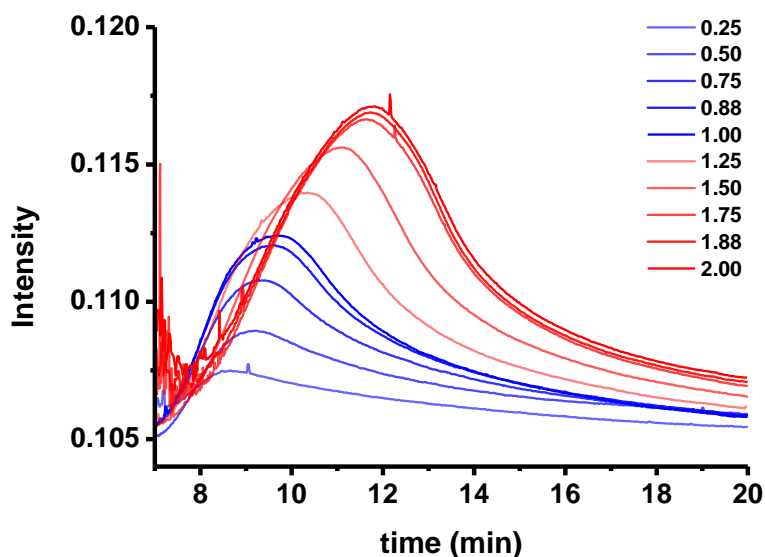


Figure S3. As4F elution curves of supramolecular polymers with different molar ratio of CB[8]/DIAV-4 characterized by static laser scattering method.

The molecular weight of supramolecular polymers with different molar ratio of CB[8]/DIAV-4 was determined by static laser scattering method, as shown in Figure S3. As the addition of CB[8], the intensity of the elution curves enhanced, accompanied with a right shift of peak values, suggesting a gradual increase of molecular weight of supramolecular polymers.

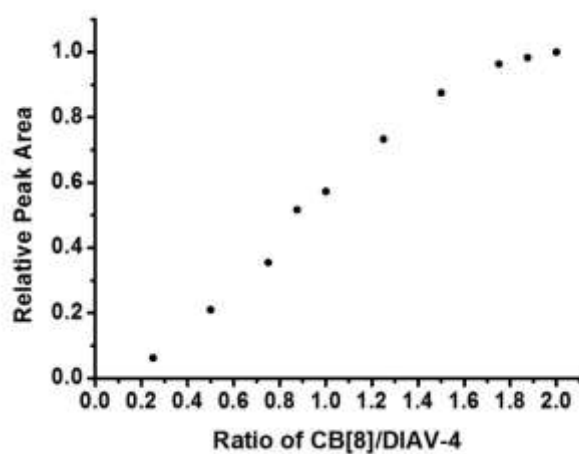


Figure S4. Changes in peak area with different molar ratio of CB[8]/DIAV-4.

The relative peak area of As4F curves was proportional to the molar ratio of CB[8]/DIAV-4 from 0 to 1.8 (Figure S4), therefore it indicated a steady increase of monomer conversion throughout the process.

Table S1. Molecular weight, polydispersity index and content of supramolecular polymers controlled by molar ratio of monomers

CB[8]/DIAV-4	M _n (kDa)	PDI	relative peak area
0.25	18.0	2.7	0.06
0.50	25.0	2.3	0.21
0.75	27.4	2.0	0.36
0.88	31.1	2.0	0.52
1.00	32.7	2.0	0.57
1.25	36.2	2.0	0.73
1.50	51.1	1.4	0.86
1.75	61.3	1.4	0.96
1.88	62.2	1.3	0.98
2.00	63.0	1.2	1.00

Changes in molecular weight, polydispersity index and content of supramolecular polymers with different molar ratio of CB[8]/DIAV-4 are summarized in Table S1. The molecular weight of supramolecular polymers could be varied from 18 to 63 kDa. The polydispersity index was finally maintained between 1.2 – 1.3 when the molar ratio of CB[8]/DIAV-4 was 2.0.

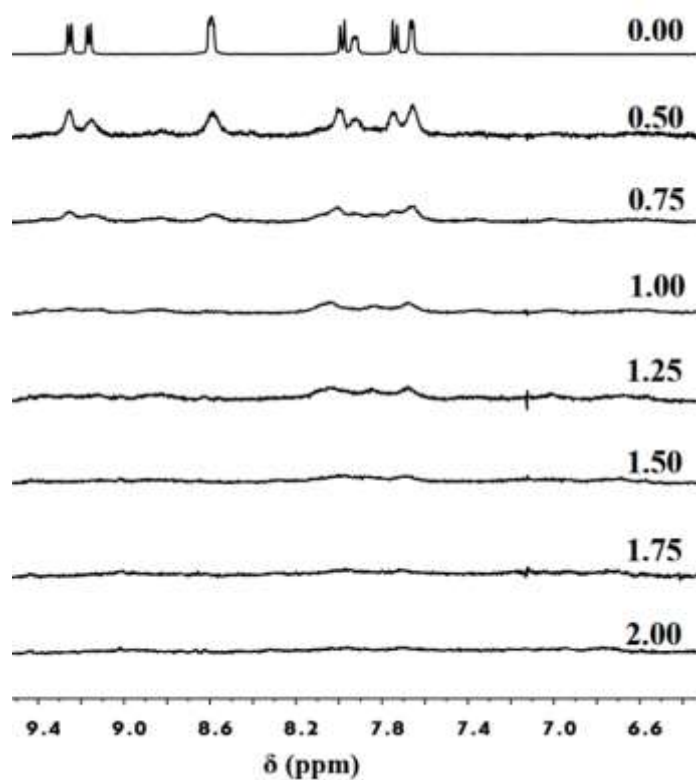


Figure S5. Changes in ^1H NMR spectra of DIAV-4 with different molar ratio of CB[8]/DIAV-4.

As the addition of CB[8], ^1H NMR signals of DIAV-4 (Figure S5) broadened and vanished, suggesting a formation of supramolecular polymers in aqueous solution.

5. Photocontrolled supramolecular polymerization

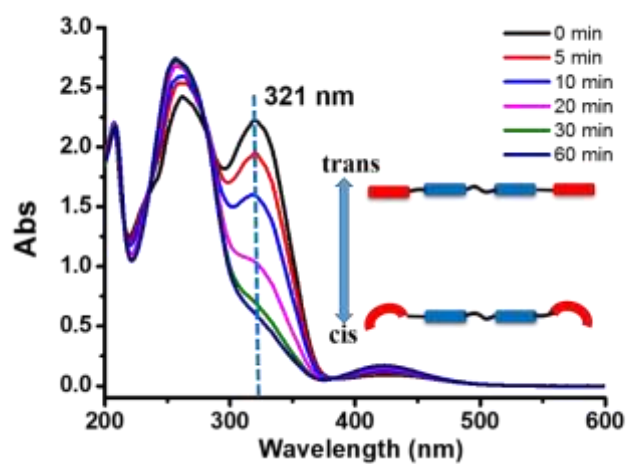


Figure S6. Changes in the UV-Vis absorption spectra of DIAV-4 solution upon irradiation of UV light at RT.

Concentration: $[\text{DIAV-4}] = 0.5 \text{ mM}$.

When a solution of DIAV-4 was irradiated by UV light, the band at 321 nm corresponding to the $\pi-\pi^*$ transition gradually decreased, until an equilibrium was reached after 60 min (Figure S6). The UV-Vis absorption spectra were recorded at intervals. Take the highest absorption intensity of band 321 nm as a benchmark, which corresponding to a full trans isomers, the relative intensity of band 321 nm from other samples were calculated.

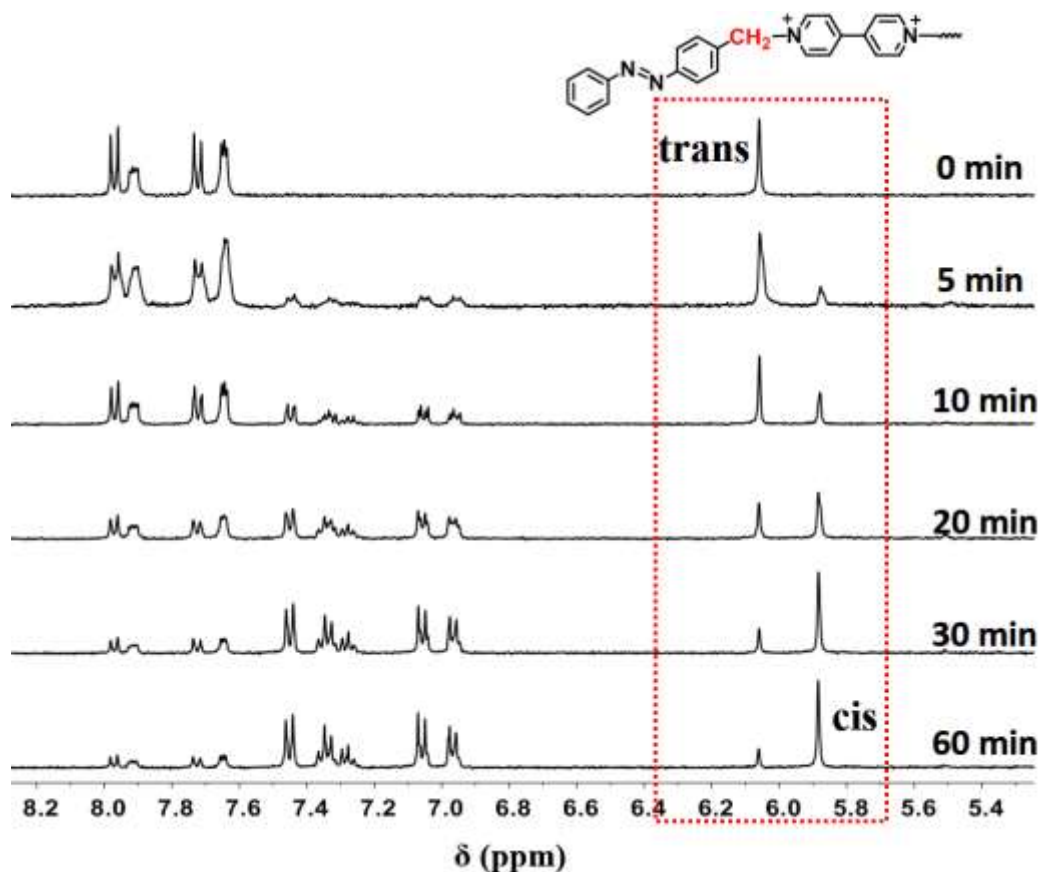


Figure S7. Changes in the ^1H NMR spectra of DIAV-4 upon irradiation of UV light at RT.

As shown in Figure S7, the azobenzene and the methyl group signals changed with the irradiation time. The peaks of methyl group were chosen to calculate the contents of two isomers in aqueous solution.

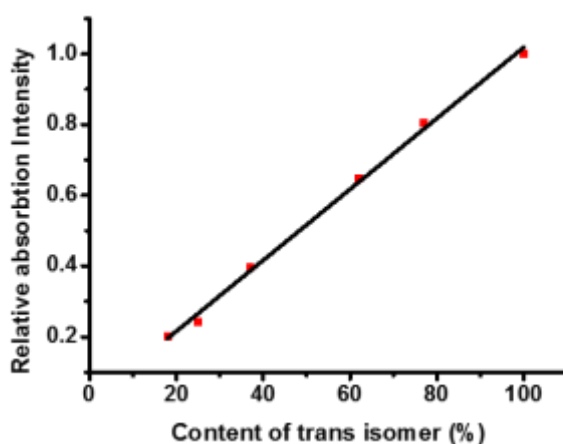


Figure S8. Linear relationship between the relative absorption intensity of 321 nm and the percent of *trans*-isomer.

A good linear relationship was found between the relative absorption intensities of band 321 nm and the contents of isomers determined by ^1H NMR (Figure S8). This result indicates that it is practicable to quantify the isomers by calculating the relative absorption intensity of band 321 through UV-Vis spectra. Considering that there is almost no change of this band for DIAV-4 monomer before and after complex with CB[8], it is reasonable to assume that this linear relationship also applicable to the corresponding supramolecular polymers.

Table S2. Molecular weight, polydispersity index and relative content of supramolecular polymers controlled by photoisomerization of azobenzene group

Content of <i>trans</i> -isomer %	M_n (kDa)	PDI	Relative Peak Area
100	62.3	1.3	1.00
86	41.5	1.5	0.96
71	33.9	1.5	0.92
60	32.5	1.6	0.88
51	31.6	1.6	0.78
40	26.9	1.9	0.57
30	18.2	2.4	0.47

Changes of molecular weight, polydispersity index and content of supramolecular polymers with different isomer ratio of azobenzene are summarized in Table S2. The molecular weight of

supramolecular polymers could be varied from 18 to 41 kDa by tuning the isomer ratio of azobenzene. It should be pointed out that only in the case of 100% of *trans*-isomers of the azobenzene, the supramolecular polymers with highest molecular weight can be obtained. DIAV-4 monomers with 100% of trans isomers were prepared by recrystallization from aqueous solution.