

Helical-Sense Matching Facilitates Supramolecular Copolymerization of Helical-Chiral Pillar[5]arenes

De-Hui Tuo,^{1,2,†} Shixin Fa,^{3,†,*} Seigo Tanaka,² Takuma Shimada,⁴ Masataka Yamashita,⁵ Yuki Togari,² Shunsuke Ohtani,² Kenichi Kato,² Kenji Urayama,⁵ Qiuyu Zhang,³ Kazuma Yasuhara,⁶ Tomoki Ogo-shi^{1,2,*}

¹WPI Nano Life Science Institute (WPI-NanoLSI), Kanazawa University, Kakuma-machi, Kanazawa, 920-1192, Japan

²Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto, 615-8510, Japan

³School of Chemistry and Chemical Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi, 710072, P.R. China

⁴Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto, 615-8510, Japan

⁵Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto, 615-8510, Japan

⁶Division of Materials Science, Nara Institute of Science and Technology, Ikoma, Nara, 630-0192, Japan

[†] These authors contributed equally.

ABSTRACT: Supramolecular polymerization using two-dimensional π -conjugated chiral monomers has been mainly demonstrated because the supramolecular polymerization can be controlled by stereocommunication through π - π stacking between the two-dimensional chiral monomers. We herein report supramolecular copolymerization utilizing three-dimensional pentahedrons with twisted helical chirality through different combinations of helical-chiral acidic and basic pillar[5]arenes as comonomers. In this case, helical-sense matching is key to facilitate the supramolecular copolymerization. Based on the unique helical chirality of the three-dimensional pillared structure of the pillar[5]arenes and alternate ion-pairing interactions between acidic and basic groups on their bilateral rims, the homochiral helical-sense matching system forms kinetically stable nanowire-shaped supramolecular copolymers, generating the supramolecular gel in high concentration. At elevated temperatures, the nanowire structure undergoes a transformation into thermodynamically stable nanoparticles, resulting in gel-to-sol transition. This process can be hindered by introducing linear guest molecules, which prohibit the units swing of pillar[5]arenes and stabilize the nanowires and supramolecular gel. By tailoring the enantiomeric ratio (e.r.) values of the chiral combinations, the helical-sense-dependent gel-to-sol transition was realized, specifically by decreasing the e.r. values. Because of helical-sense mismatching, the heterochiral system generates short, branched nanowires and presents as a turbid solution. These distinct differences reveal that the helical-sense matching between three-dimensional chiral pillar[5]arene comonomers is important for supramolecular copolymerization.

INTRODUCTION

Supramolecular polymerization has become an efficient tool in material science for its exceptional ability to organize molecular building blocks into ordered nanostructures.¹ By understanding deeper insights into the polymerization processes,² structural diversity and polymerization growth control of supramolecular polymers through kinetic pathways have been achieved by various strategies such as molecular design of monomers,³ seeded living polymerization,⁴ topologies of self-assembled structures,⁵ and copolymerization.⁶ In these supramolecular polymerization systems, incorporating chirality into monomers offers an effective approach to control the supramolecular polymerization through stereocommunication between chiral monomers.⁷ For the molecular design of monomers, two-dimensional (2D) π -conjugated molecules have been widely used in

supramolecular polymerization because continuous π - π stacking between the monomers can be used as a reliable assembly driving force.⁸ However, supramolecular polymerization utilizing three-dimensional (3D) chiral building blocks has been very rare to date because of the difficulties in introducing suitable interaction sites to generate supramolecular polymers.⁹ Additionally, the impact of stereocommunication between 3D monomers on the resulting polymeric structures remains unclear. To overcome these difficulties, using 3D highly symmetrical macrocycles is one of the good choices because the interaction sites can be installed at suitable positions to achieve the stereocommunication.¹⁰ Hence, realizing supramolecular polymerization utilizing 3D chiral macrocycles can reveal new types of supramolecular assembly principles.

Pillar[*n*]arenes, characterized by 3D pillar-shaped

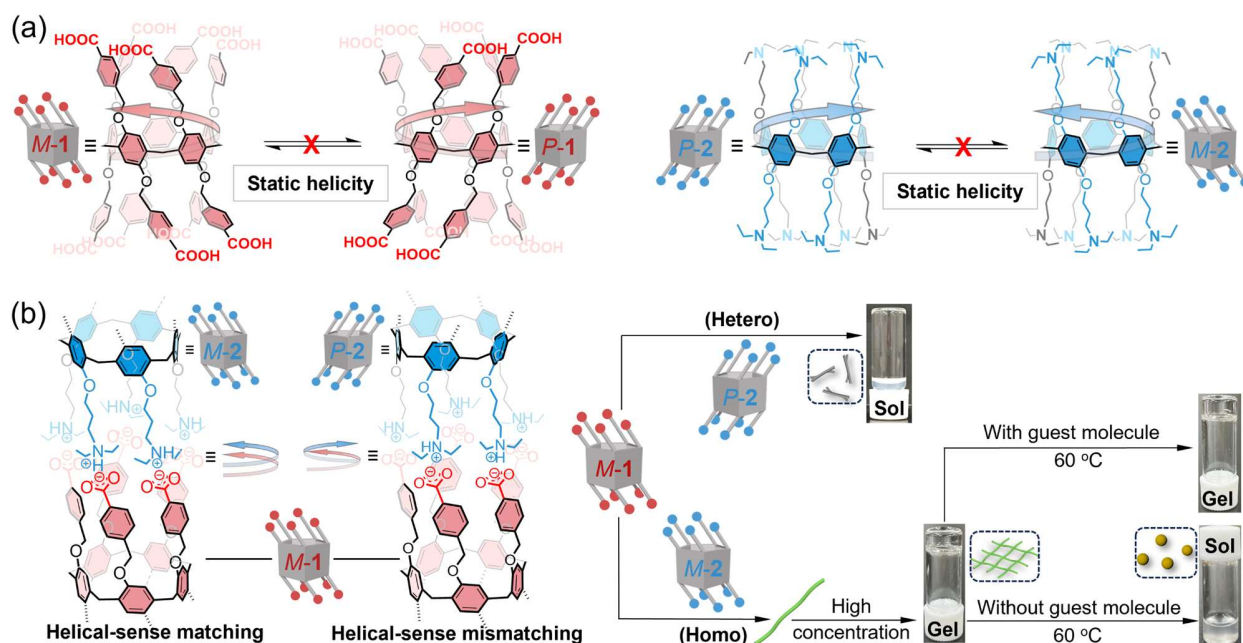


Figure 1. (a) Chemical structures of helical-chiral acidic and basic P5As. (b) Schematic representation of chirality-controlled supramolecular copolymerization by different combinations of chiral P5As.

macrocyclic structures,¹¹ exhibit unique helical chirality and excellent host–guest complexation affinity because of the directional array of units along their 3D skeletons.^{12,13} Functional groups that drive self-assembly can be installed on the bilateral rims of pillar[*n*]arenes, thus the construction of self-assembled one-dimensional organic nanotubes has been achieved.^{14–16} We previously reported the construction of discrete homochiral trimeric nanotubes through multiple ion-pairing interactions between a per-amino-pillar[5]arene (P5A) and rim-differentiated P5A penta-acid,¹⁵ in which the chiral match of P5As through ion-pair interactions selectively formed homochiral trimeric nanotubes. In this system, rotation and swinging of the units are important points to form rigid trimeric nanotubes with five-fold helical structures. Guest inclusion can also reduce the swing effect and enhance the rigidity of P5As.

In the present study, we investigated supramolecular copolymerization using 3D helical-chiral P5As as building blocks. We selected peracid-P5A **1**, bearing ten benzoic acid groups on the rims, and peramino-P5A **2**, bearing ten amino groups on the rims, as chiral comonomers (Figure 1a). Owing to these bulky substituents, their unit rotation is inhibited, thus helical-chiral *P* and *M* configurations of acidic and basic P5As can be separated by chiral HPLC. The alternate multiple ion-pairing interactions between the bilateral acid and base groups of P5As serve as the driving force to initiate supramolecular copolymerization.^{16,17}

In this copolymerization system, we discovered that helical-sense matching is key to facilitate the supramolecular copolymerization (Figure 1b). Helical-sense-matched **1** and **2** homo combination, e.g., *M-1* and *M-2*, formed kinetically stable long tubular nanowires at low concentration, and supramolecular gels at high concentration. On the other hand, helical-sense-mismatched hetero combination, e.g., *M-1* and *P-2*, produced a turbid solution due to the formation of short nanotubes with branched structures. Helical-sense

dependent gel-to-sol change was also realized by regulating the enantiomeric ratio (e.r.) of the chiral components. Moreover, the supramolecular copolymerization of the homo combination presented dynamic behavior. The homo gel was initially formed by kinetic trap and transformed into turbid solution because of the formation of thermodynamically stable nanoparticles at elevated temperature. Upon the addition of guest molecules, the reduced units swing of P5As due to host-guest complexation resulted in inhibition of nanowire-to-nanoparticle transition and gel-to-sol transformation, leading to a stabilized gel state. Hence, the host-guest complexation provides a new way to control the supramolecular copolymer formation through reducing the flexibility of the 3D macrocycles. The present results suggest that helical-chiral P5As are promising 3D chiral monomers for the construction of chiral supramolecular copolymers, which exhibit dynamic behavior controlled by host-guest complexation.

RESULT AND DISCUSSION

Optical resolution of 1

For acidic P5A **1**, the bulky substituents hinder free rotation of P5A units, resulting in fixed helical chirality, which was confirmed by ^1H NMR measurement (Figure S19). Direct optical resolution of **1** proved to be challenging because of the ten polar benzoic acid groups. To achieve the enantiomeric separation of **1**, optical resolution of the P5A ester precursor **3**, containing methyl benzoate groups, was conducted by chiral HPLC (Figure S1).^{14c} The obtained two fractions were found to be highly pure, as indicated by the HPLC traces of the reinjected fractions. The CD spectra for the two fractions presented mirror images (Figure S5), confirming their enantiomeric relationship. On the basis of the Cotton-effect signal at approximately 310 nm derived from the π - π^* transition of P5A skeletons, the first and second fractions were assigned as *M*-**3** and *P*-**3**, respectively. Enantiomeric **1** was obtained by hydrolysis of the separated enantiomers at

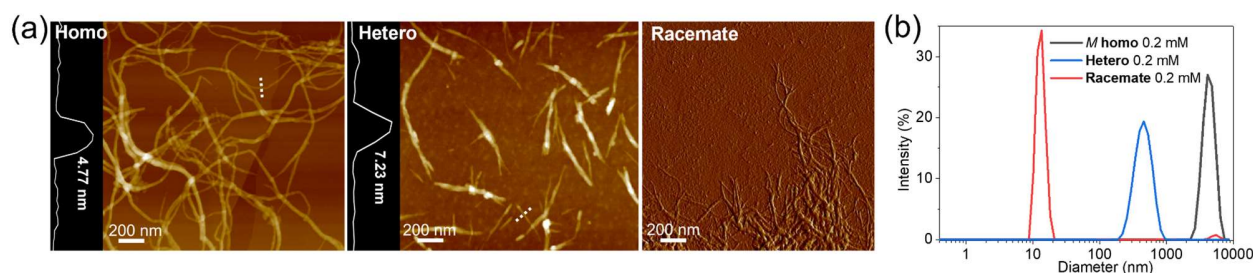


Figure 2. (a) AFM images and (b) size distributions of **homo** (*M*-1 and *M*-2), **hetero** (*M*-1 and *P*-2), and **racemate** combinations (chloroform/DMSO = 1:1 (v/v), each monomer: 0.2 mM) by DLS measurement.

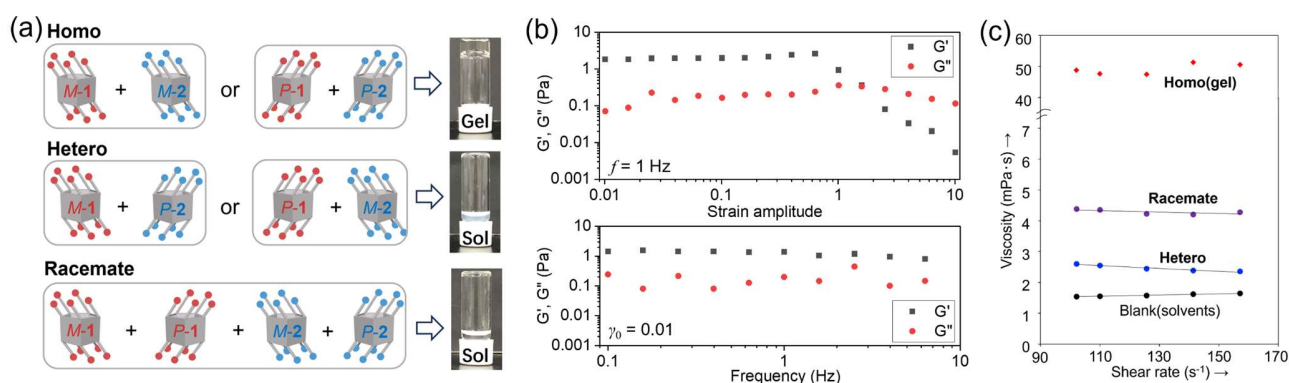


Figure 3. (a) Schematics and photographs of the **homo**, **hetero**, and **racemate** combinations. (b) Storage and loss shear modulus of homo (*M*-1 and *M*-2) as a function of strain amplitude or frequency. (c) Flow behavior of homo (*M*-1 and *M*-2), hetero (*M*-1 and *P*-2) and racemate combinations at high shear rates. (chloroform/DMSO = 1:1 (v/v), each monomer: 0.4 mM, 25 °C).

room temperature (Scheme S1). The obtained *M*-1 and *P*-1 present mirror CD spectra, and their intensities were retained for three months in a 1:1 (v/v) chloroform-DMSO mixture at room temperature, indicating high enantiomeric stability (Figure S6). The synthesis and optical resolution of peramino-P5A **2** were conducted by a previously reported method.¹⁵

Facilitation of supramolecular copolymerization by helical-sense matching

The supramolecular copolymerization behaviors of three different combinations of **1** and **2** were investigated. These were the combination of fractions with the same chirality (*M*-1 and *M*-2, or *P*-1 and *P*-2), i.e., **homo**; the combination of opposite chirality fractions (*M*-1 and *P*-2, or *P*-1 and *M*-2), i.e., **hetero**; and the combination of racemic **1** and **2**, labeled '**racemate**'. Owing to the poor solubility of **1** and the effect of solvent polarity on the strength of ion-pairing interaction (Table S1), the supramolecular copolymerization was conducted by mixing **1** in DMSO and an equivalent concentration of **2** in chloroform at a ratio of 1:1 (v/v). We found the supramolecular copolymer formation in the **homo** combination at concentrations below 0.4 mM and gel formation at a concentration of 0.4 mM.

At a concentration of 0.2 mM, the **homo** and **racemate** mixtures presented transparent solution, while the **hetero** mixtures gave a suspension. The morphologies of the three combinations presented significant differences. In the **homo** case, distinct long nanowire structures were observed by atomic force microscopy (AFM) (Figure 2a). The

smallest height profile of the nanowire observed was determined to be ~ 4.77 nm. Given the size of P5A (diameter: ca. 4.7 Å), this result indicates that the nanowires are not unimolecularly dispersed but bundled together. Conversely, the **hetero** combination exhibited short, branched nanowires. The observed smallest height profile of the short nanowires was ~ 7.23 nm, indicating that the ionic interaction between diastereomeric **1** and **2** also promoted tubular-structure formation and led to the formation of bundled nanowires, but the helical-sense mismatching hindered formation of longer nanowires. For the **racemate** combination, nanoparticles and long nanowires were observed simultaneously.

Dynamic light scattering (DLS) further revealed the supramolecular polymer formation. The **homo** mixture exhibited a sharp peak with a large average size of 4150 nm, while the **hetero** mixture displayed a broad peak with a much smaller average size of around 459 nm (Figure 2b). The **racemate** mixture showed two distinct peaks, indicating the presence of two morphologies in solution: a prominent peak averaging 13 nm and a smaller peak averaging 4800 nm. These size differences correspond well with the distinct morphologies of nanowires and nanoparticles observed in the AFM images. Furthermore, the diameters of the **homo** mixture increased with increasing concentrations (Figure S2), suggesting the supramolecular polymer growth and bundling by increasing the concentrations.

At a higher concentration of 0.4 mM (0.15% w/v), the **homo** mixture generated a transparent gel (Figure 3a) with a gel-

to-sol transition temperature (T_{gel}) of 58 °C. By shaking the **homo** gel, the gel transferred to a sol state, indicating that the gel exhibited thixotropic behavior. From TEM measurements, the nanowire structures were observed in the gel, but the nanowire transformed into nanoparticles and amorphous structures in the sol obtained by shaking (Figure S22). This result suggested that the nanowire structure is important for maintaining the gel state. The shaken sample reformed into a gel after 10 seconds to 30 minutes. However, this self-healing ability was lost after three or four repetitions.

Conversely, the **hetero** and **racemate** combinations at the concentration of 0.4 mM remained a suspension and a transparent solution, respectively (Figure 3a). The significant differences suggested that helical-sense matching of the **homo** combination is critical for the supramolecular copolymerization and gel formation, which was supported by calculations of the discrete trimeric homochiral tubular structure formation of P5As from our previous work, representing a partial structural model of the tubular nanowire.¹⁵

The formation of the gel in the **homo** combination was confirmed by dynamic mechanical analysis using strain amplitude (γ_0) and frequency (f) (Figure 3b). At sufficiently small γ_0 values, the storage shear modulus (G') remained independent of both γ_0 and f , and was significantly larger than the loss shear modulus (G''), indicating a gel state under quiescent conditions. In contrast, the **hetero** combination showed typical behavior of low-viscosity Newtonian fluid, where G'' scaled linearly with f and the phase angle (δ) approached 90° (Figure S4), reflecting a liquid behavior.

For the **homo** gel, when γ_0 exceeded approximately 1, G' decreased with increasing γ_0 , while G'' surpassed G' (Figure 3b). This thixotropic behavior suggests that the nanowire structures present in the gel state are disrupted into nanoparticles and amorphous structures under high strain, as observed by the TEM images (Figure S22). These results imply that the gel structure is primarily supported by nanowire assemblies.

Figure 3c compares the flow behavior at high shear rates for the **homo**, **racemate**, and **hetero** combinations. The viscosity of the **homo** mixture remained considerably higher than that of the other two at high shear rates, likely due to the presence of nanowires that are shortened under high strain. Rheological analysis reveals the crucial role of helical-sense matching in the formation of the supramolecular gel.

The chiral information of the supramolecular copolymerization structures was further explored by circular dichroism (CD) analysis. The **hetero** and **racemate** patterns showed almost no CD signals because enantiomeric P5A skeletons exist in the 1:1 combination (Figure S7). In the **homo** case, the supramolecular gel presented an intense CD signal at 312 nm, the intensity of which was 1.3 times higher than the sum of the CD signals of the overlapped **1** and **2** monomers (Figure 4a). The increased CD intensity is attributed to the fixed units swing upon formation of the supramolecular tubular structure.¹⁸

To monitor the supramolecular gel formation in the **homo** combination, time-dependent CD measurement was performed. Consistent CD spectra were observed with time, indicating that nanowires formed immediately upon mixing of the comonomers (Figure S8). However, vigorous shaking of

the gel resulted in obvious fluctuations of CD spectra (Figure S9), attributed to inhomogeneous structure formation, which was consistent with the TEM results (Figure S22).

Helical-sense-dependent gel formation by regulating enantiomeric ratios

To investigate the importance of helical-sense matching on supramolecular gel formation, the e.r. values of the **M homo** combination were gradually changed. As described in Figure 4b, solely decrease the e.r. value of **M-1** from 100% to 0, supramolecular gel started to become a turbid solution when the e.r. value was less than 40%. The CD intensity at around 314 nm exhibited a linear correlation with the e.r. value, indicating that combination of the remaining **homo** monomers changed linearly with e.r. value (Figure S11). Meanwhile, nanowires and nanoparticles were observed in morphology and their relative content varied with e.r. value (Figure S26). Specifically, the nanoparticles increased significantly with decreasing e.r. values, resulting in inefficient support for the gel structure and hence transformation into a turbid solution.

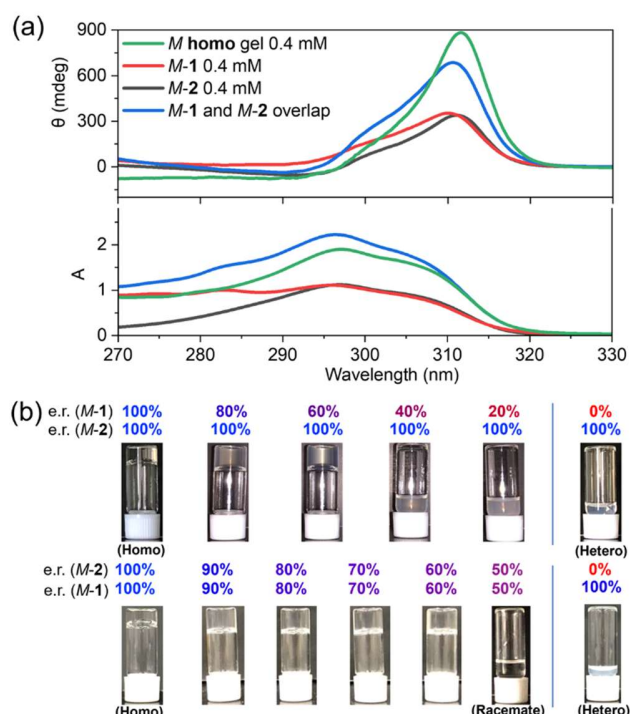


Figure 4. (a) CD and UV-Vis spectra of the **M homo** gel (chloroform/ DMSO = 1:1 (v/v), each monomer: 0.4 mM, 25 °C), **M-1** and **M-2** monomers, and the overlap spectra of **M-1** and **M-2**. (b) Helical-sense-dependent gel formation by altering the e.r. values of **M-1** and **M-2** monomers.

Changing the e.r. values of **M-1** and **M-2** simultaneously also resulted in gel-to-sol transformation. When the e.r. values were above 60%, the mixture formed the gel, while a sol state was observed when the e.r. value was decreased to 50%, i.e., the **racemate** (Figure 4b). CD intensity and e.r. value presented a similar linear correlation, indicating linear variation of the remaining **homo** combination (Figure S12). For all the measured samples, nanowires and nanoparticle structures were observed, and their relative contents varied with e.r. value. The content of nanoparticles

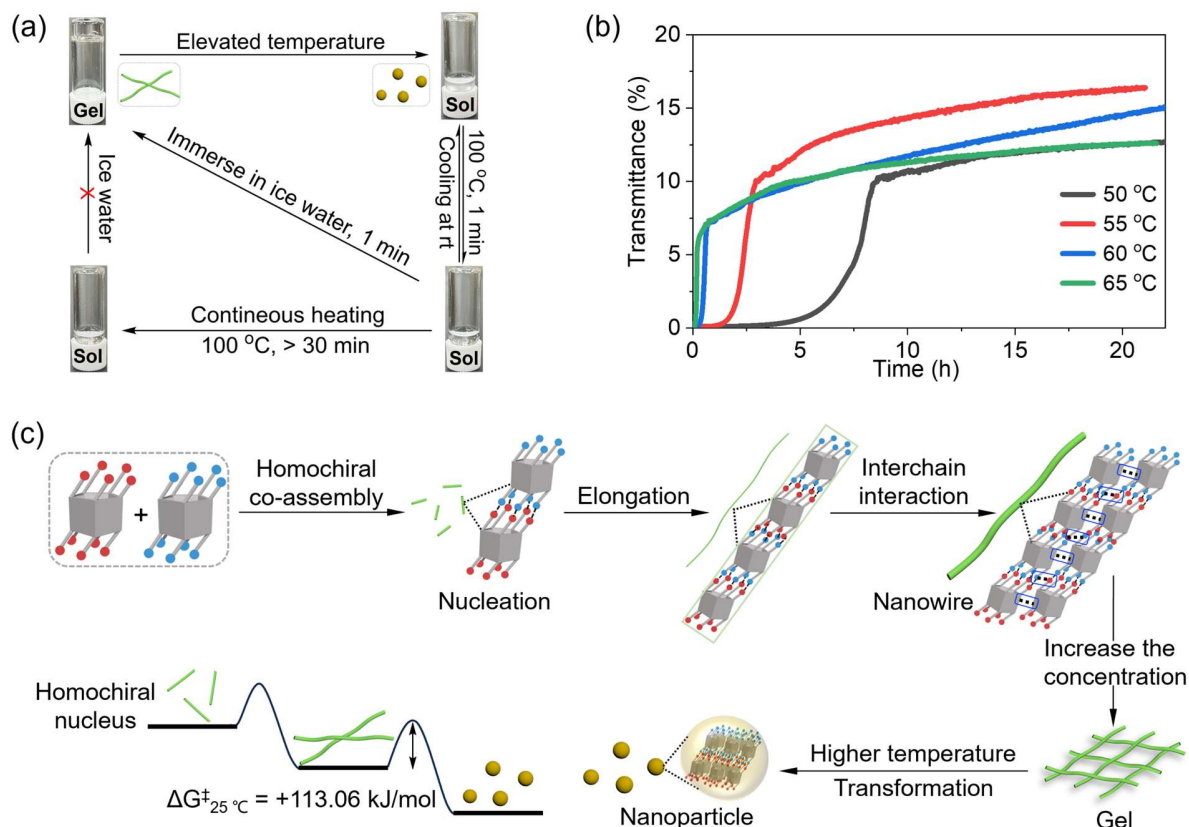


Figure 5. (a) Photographs of gel transformation. (b) Time dependence of light transmittance for the *M homo* gel (chloroform/DMSO = 1:1 (v/v), each monomer: 0.4 mM) at different temperatures. (c) Schematic representation of homo gel formation and transformation.

increased with the increase of **racemate** combination (Figure S27), resulting in the gel-to-sol transformation.

The gel characteristics depending on the e.r. values were investigated through dynamic mechanical analysis, using γ_0 as a valuable (Figure S3). The gel containing *M-1* (60% e.r.) and *M-2* (60% e.r.) exhibited solid-like behavior ($G' > G''$) at low γ_0 values whereas it transitioned to a liquid-like state ($G'' > G'$) at higher γ_0 , similar to the behavior observed in the gel formed from the **homo** combination. However, for the gel with a 60% e.r. value, a linear modulus independent of γ_0 was not clearly observed, even at extremely small γ_0 values less than 0.1. In addition, the reduction in G' with increasing γ_0 was more gradual than that observed in the gel in the **homo** combination. These differences are likely due to the inhomogeneous microstructure, consisting of a mixture of nanotubes and particles, as supported by SEM images (Figure S27).

Dynamic transformation behavior in homo combination

The **homo** gel sample transformed into a turbid solution when kept at temperatures over 30 °C for several days (Figure 5a). The resultant solution showed a quite weak CD signal (Figure S10) due to the precipitated nanoparticles (Figure S24b). This process can be facilitated by elevating the temperatures and monitored by SEM measurements, during which the nanowire structures in the gel state completely transformed into nanoparticles in the sol state (Figure S25). Even in the supramolecular polymer formed by the **homo** mixture at a low concentration (0.05 mM), a noticeable

change from a transparent solution to a turbid one was observed. The change came from the transformation from nanowires to nanoparticles, which was monitored by SEM and time-dependent of light transmittance measurements. (Figures S23 and S31). These results indicate that the nanowire structure is kinetically favored while the nanoparticle structure is the thermodynamically stable product.

Considering that the turbidity changes during the transformation, the time-dependence of the light transmittance at 296 nm was measured on a temperature-controlled UV-Vis spectrometer to investigate the transformation process of the gel in more detail. In the initial stage, the transmittance strength showed little change, then there was an abrupt increase as the nanoparticles precipitate until the transmittance signal approached equilibrium (Figure 5b). This process was facilitated by higher temperatures, at which the equilibrium time was significantly reduced. Although the transmittance strength at the equilibrium state was different for different batches of samples, the transformation tendency was similar at the setting temperatures. The Gibbs energy of activation at 25 °C ($\Delta G^\ddagger_{25^\circ\text{C}}$) for the gel was determined to be 113.06 ± 24.09 kJ/mol from the Eyring plot (Figure S18).

The generated nanoparticles were quite stable, thus the gel state cannot be recovered by vigorous shanking or long-time sonication. The gel was only recovered by heating the sample under 100 °C for 1 minute to completely dissolve the nanoparticles and immediately immersing the sample in ice water (~ 5 °C) for 1 minute (Figure 5a). This process can be repeated at least eight times before the sample becomes a

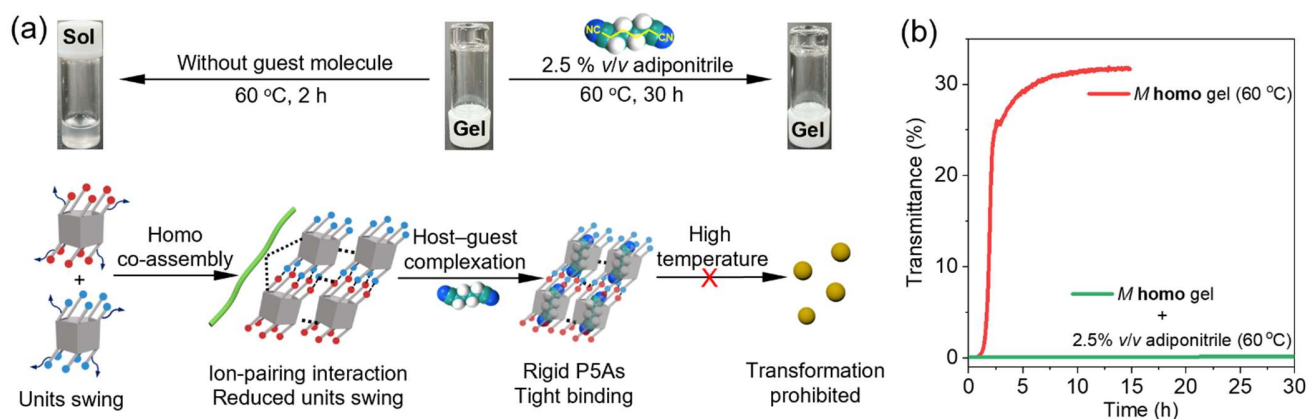


Figure 6. (a) Photographic and schematic representations of gel transformation by adding guest molecules. (b) Time-dependent light transmittance of the *M* **homo** gel (chloroform/DMSO = 1:1 (v/v), each monomer: 0.4 mM) with and without guest molecules.

clear solution because racemization occurs at high temperature (Figures S13–S15), indicating that the gel formation and recovery are kinetically and helical-sense-dependent processes.

Based on the observed morphologies and the dynamic transformation process of the assembled structures, the probable supramolecular polymerization and gelation processes are proposed (Figure 5c), in which helical-sense matching and helical-sense mismatching of chiral comonomers significantly affect the supramolecular copolymerization. When **1** and **2** are mixed in **homo** combination, the two P5As would form oligomeric tubular structures that act as nuclei. The helical-sense matching between the two monomers and multiple ion-pairing interactions ensures the rapid linear propagation of supramolecular copolymerization. The generated kinetically stable nanowires bundle together through electrostatic interactions and π - π stacking. At a high concentration of 0.4 mM, the nanowires further bundle and form crosslinking network structures, resulting in the gel formation. However, high temperatures facilitate dissociation of the nanowires and transformation into thermo-dynamically stable nanoparticles, which may result from the units swing of P5As. In the **hetero** and **racemate** systems, helical-sense matching and mismatching also significantly affect the supramolecular polymerization and transformation (details are shown in Figure S28).

Host-guest effect on the transformation in homo combination

We hypothesized that the unit swings of P5As at elevated temperatures lead to flexible 3D macrocycles and cause the nanowires to nanoparticles transformation and gel-to-sol transition. Thus, adding guest molecules can inhibit the unit swing by including the guest molecule in the cavity, resulting in the formation of rigid P5As and kinetically trapped nanowires and gels. Since P5As are ideal host macrocycles for linear guest molecules,¹⁹ a series of linear guest molecules were added to **homo** gel samples. Upon adding an excess of adiponitrile (2.5% v/v), 1,2-dichloroethane (DCE, 2.5% v/v), or 1,4-dibromobutane (DBB, 2.5% v/v), which are known to be good guest molecules for P5As, into the gel samples, continuous increases of CD intensity were observed (Figure S16). These increased CD signals indicate that the nanotubular structures remain intact and that the

guest molecules enter the cavities freely through host-guest complexation, resulting in reduced unit swing of the P5As.²⁰ The stability of the supramolecular gel after guest complexation was further demonstrated at elevated temperatures. Comparing with the rapid gel-to-sol transformation at 60 °C, adding adiponitrile (2.5% v/v, 275 eq.) made the gel quite stable (Figure 6a). Meanwhile, the time-dependent light transmittance strengths of the gel sample containing adiponitrile showed no change at 60 °C for 30 hours (Figure 6b). In a different process, the supramolecular gel in the homo combination was prepared by mixing pre-formed adiponitrile-*M*-**1** complex with adiponitrile-*M*-**2** complex (Figure S17). In this case, the supramolecular gel also formed, and showed no change to a sol state at 60 °C (Figure S30). These results indicate that the reduction in unit swing of the P5As by guest complexation increases the rigidity of P5As, and further stabilizes gel structures by strengthening the ion-pairing interaction. Even by standing the gel sample containing adiponitrile (2.5% v/v) at 100 °C for 1 minute and then cooling it down at room temperature, the sample remained almost transparent, while the gel sample without guest molecules became completely turbid, indicating that host-guest complexation greatly hindered the transformation (Figure S29). The complexation-induced structural stabilization was also observed in the supramolecular polymer formed at the low concentration (0.05 mM). In the presence of adiponitrile, the transparent solution containing nanowires in the **homo** combination remained transparent even by heating at 60 °C, while the transformation from transparent to turbid occurred in the absence of adiponitrile (Figure S31). The results clearly show that host-guest complexation between P5As and linear guest molecules stabilizes the nanowire structures, thereby reinforcing the supramolecular gel composed of these nanowires.

CONCLUSIONS

In conclusion, we have developed a new chiral supramolecular copolymerization system utilizing the unique 3D helical-chiral P5As. The copolymerization process, driven by multiple ion-pairing interactions, shows distinct chiral discrimination through helical-sense matching and mismatching interactions for different combinations of monomers. Specifically, the homo combination results in long tubular nanowires in low concentration because of helical-sense matching, and eventually forms supramolecular gel at high

concentration. The high e.r. values, i.e., > 60%, required to form the gel also indicate the importance of the helical-sense matching. The hetero combination presents short branched nanowires owing to helical-sense mismatching of the P5A monomers, while the supramolecular assembly of the racemate presents the mixture of nanowires and nanoparticles. This work demonstrates that connecting the comonomers to make smooth helical structures by homochiral combination with higher e.r. values is key to form the supramolecular polymer and gel, which is quite different from other supramolecular polymer and gel systems demonstrated by the planar π molecules.²¹ Despite the well-studied supramolecular polymerization using host–guest conjugates as monomers,²² this work further indicates that host–guest complexation offers an additional strategy for regulating the supramolecular copolymerization pathway by reducing flexibility of the macrocyclic comonomers.

In biological systems, supramolecular copolymerizations have been observed by using functionalized nanotubular proteins.²³ The nanotubular proteins have tubular structures and interactions sites on the both rims of the tubes, which are quite similar structures of cationic and anionic P5As used in this study. Therefore, the present work may lead to our further understanding of supramolecular copolymerization in biological systems and construction of biomimetic nanomaterials by chiral supramolecular copolymerization of tubular helical-chiral P5As.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, Chiral HPLC traces, DLS, Rheological analysis, NMR, UV–Vis, CD spectra, SEM, TEM and Eyring plots (PDF).

AUTHOR INFORMATION

Corresponding Author

*Shixin Fa

Email: sfa@nwpu.edu.cn

*Tomoki Ogoshi

Email: ogoshi.tomoki.3s@kyoto-u.ac.jp

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) De Greef, T. F. A.; Smulders, M. M. J.; Wolfs, M.; Schenning, A.; Sijbesma, R. P.; Meijer, E. W. Supramolecular Polymerization. *Chem. Rev.* **2009**, *109*, 5687–5754. (b) Aida, T.; Meijer, E. W.; Stupp, S. I. Functional Supramolecular Polymers. *Science* **2012**, *335*,

813–817. (c) Aida, T.; Meijer, E. W. Supramolecular Polymers–We’ve Come Full Circle. *Isr. J. Chem.* **2020**, *60*, 33–47. (d) Hashim, P. K.; Bergueiro, J.; Meijer, E. W.; Aida, T. Supramolecular Polymerization: A Conceptual Expansion for Innovative Materials. *Prog. Polym. Sci.* **2020**, *105*, 101250. (e) Sun, P.; Qin, B.; Xu, J. F.; Zhang, X. Supramonomers for Controllable Supramolecular Polymerization and Renewable Supramolecular Polymeric Materials. *Prog. Polym. Sci.* **2022**, *124*, 101486. (2) (a) Korevaar, P. A.; George, S. J.; Markvoort, A. J.; Smulders, M. M. J.; Hilbers, P. A. J.; Schenning, A. P. H. J.; de Greef, T. F. A.; Meijer, E. W. Pathway Complexity in Supramolecular Polymerization. *Nature* **2012**, *481*, 492–496. (b) Kulkarni, C.; Meijer, E. W.; Palmans, A. R. A. Cooperativity Scale: A Structure–Mechanism Correlation in the Self-Assembly of Benzene-1,3,5-tricarboxamides. *Acc. Chem. Res.* **2017**, *50*, 1928–1936. (c) Wehner, M.; Würthner, F. Supramolecular Polymerization through Kinetic Pathway Control and Living Chain Growth. *Nat. Rev. Chem.* **2020**, *4*, 38–53. (d) Sorrenti, A.; Leira, I. J.; Markvoort, A. J.; De Greef, T. F. A.; Hermans, T. M. Non-Equilibrium Supramolecular Polymerization. *Chem. Soc. Rev.* **2017**, *46*, 5476–5490. (e) Fukui, T.; Kawai, S.; Fujinuma, S.; Matsushita, Y.; Yasuda, T.; Sakurai, T.; Seki, S.; Takeuchi, M.; Sugiyasu, K. Control over Differentiation of a Metastable Supramolecular Assembly in One and Two Dimensions. *Nat. Chem.* **2017**, *9*, 493–499. (f) Matern, J.; Dorca, Y.; Sánchez, L.; Fernandez, G. Revisiting Complex Supramolecular Polymerization under Kinetic and Thermodynamic Control. *Angew. Chem., Int. Ed.* **2019**, *58*, 16730–16740. (g) Zhao, W.; Qiao, B.; Tropp, J.; Pink, M.; Azoulay, J. D.; Flood, A. H. Linear Supramolecular Polymers Driven by Anion–Anion Dimerization of Difunctional Phosphonate Monomers Inside Cyanostar Macrocycles. *J. Am. Chem. Soc.* **2019**, *141*, 4980–4989. (h) Sen, S. K.; Mukhopadhyay, R. D.; Choi, S.; Hwang, I.; Kim, K. Spatiotemporal segregation of chiral supramolecular polymers. *Chem* **2023**, *9*, 624–636. (i) Talens, V. S.; Davis, J.; Wu, C.-H.; Wen, Z.; Lauria, F.; Gupta, K. B. S. S.; Rudge, R.; Boraghi, M.; Hagemeijer, A.; Trinh, T. T.; Englebienne, P.; Voets, P. K.; Wu, J. I.; Kietlyka, R. E. *J. Am. Chem. Soc.* **2020**, *142*, 19907–19916. (3) (a) Ogi, S.; Fukui, T.; Jue, M. L.; Takeuchi, M.; Sugiyasu, K. Kinetic Control over Pathway Complexity in Supramolecular Polymerization through Modulating the Energy Landscape by Rational Molecular Design. *Angew. Chem., Int. Ed.* **2014**, *53*, 14363–14367. (b) Ogi, S.; Stepanenko, V.; Thein, J.; Würthner, F. Impact of Alkyl Spacer Length on Aggregation Pathways in Kinetically Controlled Supramolecular Polymerization. *J. Am. Chem. Soc.* **2016**, *138*, 670–678. (c) Matern, J.; Fernández, Z.; Bäumer, N.; Fernández, G. Expanding the Scope of Metastable Species in Hydrogen Bonding-Directed Supramolecular Polymerization. *Angew. Chem., Int. Ed.* **2022**, *61*, e202203783. (4) (a) Ogi, S.; Sugiyasu, K.; Manna, S.; Samitsu, S.; Takeuchi, M. Living Supramolecular Polymerization Realized through a Biomimetic Approach. *Nat. Chem.* **2014**, *6*, 188–195. (b) Endo, M.; Fukui, T.; Jung, S. H.; Yagai, S.; Takeuchi, M.; Sugiyasu, K. Photoregulated Living Supramolecular Polymerization Established by Combining Energy Landscapes of Photo Isomerization and Nucleation–Elongation Processes. *J. Am. Chem. Soc.* **2016**, *138*, 14347–14353. (c) Kang, J.; Miyajima, D.; Mori, T.; Inoue, Y.; Itoh, Y.; Aida, T. A Rational Strategy for The Realization of Chain-Growth Supramolecular Polymerization. *Science* **2015**, *347*, 646–651. (d) Mukhopadhyay, R. D.; Ajayaghosh, A. Living Supramolecular Polymerization. *Science* **2015**, *349*, 241–242. (e) Ogi, S.; Stepanenko, V.; Sugiyasu, K.; Takeuchi, M.; Würthner, F. Mechanism of Self-Assembly Process and Seeded Supramolecular Polymerization of Perylene Bisimide Organogelator. *J. Am. Chem. Soc.* **2015**, *137*, 3300–3307. (f) Wagner, W.; Wehner, M.; Stepanenko, V.; Würthner, F. Supramolecular Block Copolymers by Seeded Living Polymerization of Perylene Bisimides. *J. Am. Chem. Soc.* **2019**, *141*, 12044–12054. (g) Shyshov, O.; Haridas, S. V.; Pesce, L.; Qi, H.; Gardin, A.; Bochicchio, D.; Kaiser, U.; Pavan, G. M.; von Delius, M. Living Supramolecular Polymerization of Fluorinated Cyclohexanes. *Nat. Commun.* **2021**, *12*, 3134. (h) Khanra, P.; Rajdev, P.; Das, A. Seed-Induced Living Two-Dimensional (2D) Supramolecular Polymerization in Water: Implications on Protein Adsorption and Enzyme Inhibition. *Angew. Chem., Int. Ed.* **2024**, *63*, e202400486.

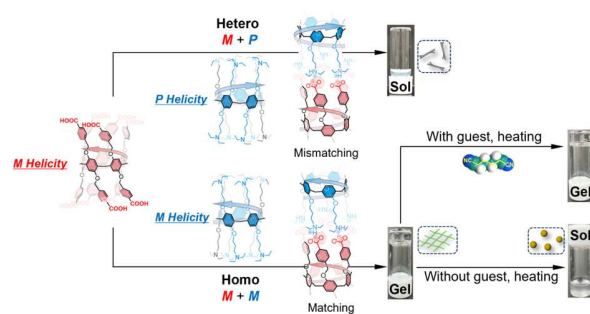
- (5) (a) Suzuki, A.; Aratsu, K.; Datta, S.; Shimizu, N.; Takagi, H.; Haruki, R.; Adachi, S. I.; Hollamby, M.; Silly, F.; Yagai, S. Topological Impact on the Kinetic Stability of Supramolecular Polymers. *J. Am. Chem. Soc.* **2019**, *141*, 13196–13202. (b) Datta, S.; Kato, Y.; Higashiharaguchi, S.; Aratsu, K.; Isobe, A.; Saito, T.; Prabhu, D. D.; Kitamoto, Y.; Hollamby, M. J.; Smith, A. J.; Dalglish, R.; Mahmoudi, N.; Pesce, L.; Perego, C.; Pavan, G. M.; Yagai, S. Self-Assembled Poly-Catenanes from Supramolecular Toroidal Building Blocks. *Nature* **2020**, *583*, 400–405. (c) Sasaki, N.; Mabesoone, M. F. J.; Kikkawa, J.; Fukui, T.; Shioya, N.; Shimoaka, T.; Hasegawa, T.; Takagi, H.; Haruki, R.; Shimizu, N.; Adachi, S. I.; Meijer, E. W.; Takeuchi, M.; Sugiyasu, K. Supramolecular Double-Stranded Archimedean Spirals and Concentric Toroids. *Nat. Commun.* **2020**, *11*, 3578.
- (6) (a) Besenius, P. Controlling Supramolecular Polymerization Through Multicomponent Self-Assembly. *Polym. Chem.* **2017**, *55*, 34–78. (b) Adelizzi, B.; Van Zee, N. J.; de Windt, L. N. J.; Palmans, A. R. A.; Meijer, E. W. Future of Supramolecular Copolymers Unveiled by Reflecting on Covalent Copolymerization. *J. Am. Chem. Soc.* **2019**, *141*, 6110–6121. (c) Takahashi, S.; Yagai, S. Harmonizing Topological Features of Self-Assembled Fibers by Rosette-Mediated Random Supramolecular Copolymerization and Self-Sorting of Monomers by Photo-Cross Linking. *J. Am. Chem. Soc.* **2022**, *144*, 13374–13383. (d) Frisch, H.; Fritz, E.-C.; Stricker, F.; Schmäser, L.; Spitzer, D.; Weidner, T.; Ravoo, B. J.; Besenius, P. Kinetically Controlled Sequential Growth of Surface-Grafted Chiral Supramolecular Copolymers. *Angew. Chem., Int. Ed.* **2016**, *55*, 7242–7246. (e) Ueda, M.; Aoki, T.; Akiyama, T.; Nakamuro, T.; Yamashita, K.; Yanagisawa, H.; Nureki, O.; Kikkawa, M.; Nakamura, E.; Aida, T.; Itoh, Y. Alternating Heterochiral Supramolecular Copolymerization. *J. Am. Chem. Soc.* **2021**, *143*, 5121–5126. (f) Adelizzi, B.; Aloï, A.; Markvoort, A. J.; Eikelder, H. M. M. T.; Voets, I. K.; Palmans, A. R. A.; Meijer, E. W. Supramolecular Block Copolymers under Thermodynamic Control. *J. Am. Chem. Soc.* **2018**, *140*, 7168–7175. (g) Sarkar, A.; Sasmal, R.; Das, A.; Venugopal, A.; Agasti, S. S.; George, S. J. Tri-component Supramolecular Multiblock Copolymers with Tunable Composition via Sequential Seeded Growth. *Angew. Chem., Int. Ed.* **2021**, *60*, 18209–18216. (h) Khanra, P.; Singh, A. K.; Roy, L.; Das, A. Pathway Complexity in Supramolecular Copolymerization and Blocky Star Copolymers by a Hetero-Seeding Effect. *J. Am. Chem. Soc.* **2023**, *145*, 5270–5284.
- (7) (a) Van Gestel, J.; Palmans, A. R. A.; Titulaer, B.; Vekemans, J. A. J. M.; Meijer, E. W. “Majority-Rules” operative in Chiral Columnar Stacks of C3-Symmetrical Molecules. *J. Am. Chem. Soc.* **2005**, *127*, 5490–5494. (b) Jin, W.; Fukushima, T.; Niki, M.; Kosaka, A.; Ishii, N.; Aida, T. Self-Assembled Graphitic Nanotubes with One-Handed Helical Arrays of a Chiral Amphiphilic Molecular Graphene. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102*, 10801–10806. (c) Mayoral, M. J.; Guilleme, J.; Calbo, J.; Aragó, J.; Aparicio, F.; Ortí, E.; Torres, T.; González-Rodríguez, D. Dual-Mode Chiral Self Assembly of Cone-shaped Subphthalocyanine Aromatics. *J. Am. Chem. Soc.* **2020**, *142*, 21017–21031. (d) Sarkar, S.; Sarkar, A.; Som, A.; Agasti, S. S.; George, S. J. Stereoselective Primary and Secondary Nucleation Events in Multi-component Seeded Supramolecular Polymerization. *J. Am. Chem. Soc.* **2021**, *143*, 11777–11787. (e) Liao, R.; Wang, F.; Guo, Y.; Han, Y.; Wang, F. Chirality-Controlled Supramolecular Donor–Acceptor Copolymerization with Distinct Energy Transfer Efficiency. *J. Am. Chem. Soc.* **2022**, *144*, 9775–9784. (f) Oh, J. S.; Kim, K. Y.; Kim, M.; Kim, S.; Jung, S. H.; Jung, J. H. Chiral Supramolecular Multiblock Copolymerization Accompanying Chirality Transfer in Heterostructures via Living Chain Growth. *Angew. Chem., Int. Ed.* **2023**, *62*, e202300913. (g) Sarkar, A.; Sasmal, R.; Empereurmot, C.; Boichicchio, D.; Kompella, S. V. K.; Sharma, K.; Dhiman, S.; Sundaram, B.; Agasti, S. S.; Pavan, G. M.; George, S. J. Self-Sorted, Random, and Block Supramolecular Copolymers via Sequence Controlled, Multi-component Self-Assembly. *J. Am. Chem. Soc.* **2020**, *142*, 7606–7617. (8) (a) Hoebe, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. About Supramolecular Assemblies of π -conjugated Systems. *Chem. Rev.* **2005**, *105*, 1491–1496. (b) Ghosh, G.; Dey, P.; Ghosh, S. Controlled Supramolecular Polymerization of π -Systems. *Chem. Commun.* **2020**, *56*, 6757–6769. (c) Greciano, E. E.; Calbo, J.; Buendia, J.; Cerda, J.; Arago, J.; Ortí, E.; Sánchez, L. Decoding the Consequences of Increasing the Size of Self-Assembling Tricarboxamides on Chiral Amplification. *J. Am. Chem. Soc.* **2019**, *141*, 7463–7472. (d) Su, H.; Jansen, S. A. H.; Schnitzer, T.; Weyandt, E.; Rösch, A. T.; Liu, J.; Vantomme, G.; Meijer, E. W. Unraveling the Complexity of Supramolecular Copolymerization Dictated by Triazine-Benzene Interactions. *J. Am. Chem. Soc.* **2021**, *143*, 17128–17135. (9) Sato, K.; Itoh, Y.; Aida, T. Homochiral Supramolecular Polymerization of Bowl-shaped Chiral Macrocycles in Solution. *Chem. Sci.* **2014**, *5*, 136–140. (10) (a) Han, X.-N.; Han, Y.; Chen, C.-F. Pagoda[4]arene and i-Pagoda[4]arene. *J. Am. Chem. Soc.* **2020**, *142*, 8262–8269. (b) Han, X.-N.; Li, P. F.; Han, Y.; Chen, C.-F. Enantiomeric Water-Soluble Octopus[3]arenes for Highly Enantioselective Recognition of Chiral Ammonium Salts in Water. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202202527. (c) Wang, L. L.; Chen, Z.; Liu, W. E.; Ke, H.; Wang, S. H.; Jiang, W. Molecular Recognition and Chirality Sensing of Epoxides in Water Using Endo-Functionalized Molecular Tubes. *J. Am. Chem. Soc.* **2017**, *139*, 8436–8439. (d) Chai, H.; Chen, Z.; Wang, S.-H.; Quan, M.; Yang, L.-P.; Ke, H.; Jiang, W. Enantioselective Recognition of Neutral Molecules in Water by a Pair of Chiral Biomimetic Macrocyclic Receptors. *CCS Chem.* **2020**, *2*, 440–452. (e) Tong, S.; Li, J.-T.; Liang, D.-D.; Zhang, Y.-E.; Feng, Q.-Y.; Zhang, X.; Zhu, J.; Wang, M.-X. Catalytic enantioselective Synthesis and Switchable Chiroptical Property of Inherently Chiral Macrocycles. *J. Am. Chem. Soc.* **2020**, *142*, 14432–14436. (f) Sato, S.; Yoshii, A.; Takahashi, S.; Furumi, S.; Takeuchi, M.; Isobe, H. Chiral Intertwined Spirals and Magnetic Transition Dipole Moments Dictated by Cylinder Helicity. *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 13097–13101. (g) Hasegawa, M.; Nojima, Y.; Mazaki, Y. Circularly Polarized Luminescence in Chiral π -Conjugated Macrocycles. *ChemPhotoChem* **2021**, *5*, 1042–1058. (h) Xue, Y.; Shi, Y.; Chen, P. Circularly Polarized Luminescent π -Conjugated Chiral Nanorings and Nanobelts. *Adv. Optical Mater.* **2024**, *12*, 2303322. (i) Yu, Y.; Hu, Y.; Ning, C.; Shi, W.; Yang, A.; Zhao, Y.; Cao, Z.-Y.; Xu, Y.; Du, P. BINOL-Based Chiral Macrocycles and Cages. *Angew. Chem., Int. Ed.* **2024**, *63*, No. e202407034. (11) (a) Ogoshi, T.; Kanai, S.; Fujinami, S.; Yamagishi, T.; Nakamoto, Y. *para*-Bridged Symmetrical Pillar[5]arenes: Their Lewis Acid Catalyzed Synthesis and Host–Guest Property. *J. Am. Chem. Soc.* **2008**, *130*, 5022–5023. (b) Strutt, N. L.; Zhang, H. C.; Schneebeli, S. T.; Stoddart, J. F. Functionalizing Pillar[n]arenes. *Acc. Chem. Res.* **2014**, *47*, 2631–2642. (c) Si, W.; Xin, P.; Li, Z.-T.; Hou, J.-L. Tubular Unimolecular Transmembrane Channels: Construction Strategy and Transport Activities. *Acc. Chem. Res.* **2015**, *48*, 1612–1619. (d) Jie, K.; Zhou, Y.; Li, E.; Huang, F. Nonporous Adaptive Crystals of Pillararenes. *Acc. Chem. Res.* **2018**, *51*, 2064–2072. (e) Ogoshi, T.; Yamagishi, T.; Nakamoto, Y. Pillar-shaped Macrocyclic Hosts Pillar[n]arenes: New Key Players for Supramolecular Chemistry. *Chem. Rev.* **2016**, *116*, 7937–8002. (f) Li, Z.; Yang, Y.-W. Functional Materials with Pillarene Struts. *Acc. Mater. Res.* **2021**, *2*, 292–305. (g) Wang, K.; Tian, X.; Jordan, J. H.; Velmurugan, K.; Wang, L.; Hu, X.-Y. The Emerging Applications of Pillarene Architectures in Supramolecular Catalysis. *Chin. Chem. Lett.* **2022**, *33*, 89–96. (h) Tuo, D.-H.; Shi, T.-H.; Ohtani, S.; Ogoshi, T. Responsive Pillar[n]arene Materials. *Responsive Mater.* **2024**, *2*, e20230024. (12) (a) Fa, S.; Kakuta, T.; Yamagishi, T.; Ogoshi, T. Conformation and Planar Chirality of Pillar[n]arenes. *Chem. Lett.* **2019**, *48*, 1278–1287. (b) Shi, C.; Li, H.; Shi, X.; Zhao, L.; Qiu, H. Chiral Pillar[n]arenes: Conformation Inversion, Material Preparation and Applications. *Chin. Chem. Lett.* **2022**, *33*, 3613–3622. (c) Kato, K.; Fa, S.; Ogoshi, T. Alignment and Dynamic Inversion of Planar Chirality in Pillar[n]arenes. *Angew. Chem., Int. Ed.* **2023**, *62*, e202308316. (d) Shi, T.-H.; Ohtani, S.; Kato, K.; Fa, S.; Ogoshi, T. Host–Guest Behavior of Pillar[n]arene based Supramolecular Assemblies. *Trends Chem.* **2023**, *5*, 537–550. (e) Sala, P. D.; Calice, U.; Iuliano, V.; Geremia, S.; Hickey, N.; Belviso, S.; Summa, F. F.; Monaco, G.; Gaeta, C.; Superchi, S. Chirality sensing of cryptochiral guests with prism[n]arenes. *Chem. -Eur. J.* **2024**, *30*, e202401625. (13) The chirality of pillar[n]arenes is generally defined as planar chirality (pR and pS), which described the chirality of the repeating unit. Hence, the chirality of pillar[5]arene can be described as (pR , pR , pR , pR). Meanwhile, considering the helical alignment of the

substituents, helicity (*P* and *M*) can also be used to describe the chirality of the whole structure. To unify the terminology in this article, we used helicity for the chirality of pillar[5]arenes.

- (14) (a) Fa, S.; Sakata, Y.; Akine, S.; Ogoshi, T. Non-Covalent Interactions Enable the Length-Controlled Generation of Discrete Tubes Capable of Guest Exchange. *Angew. Chem., Int. Ed.* **2020**, *59*, 9309–9313. (b) Strilets, D.; Fa, S.; Hardiagon, A.; Baaden, M.; Ogoshi, T.; Barboiu, M. Biomimetic Approach for Highly Selective Artificial Water Channels Based on Tubular Pillar[5]arene Dimers. *Angew. Chem., Int. Ed.* **2020**, *59*, 23213–23219. (c) Andrei, I.-M.; Strilets, D.; Fa, S.; Baaden, M.; Ogoshi, T.; Barboiu, M. Combinatorial Screening of Water/Proton Permeation of Self-Assembled Pillar[5]arene Artificial Water Channel Libraries. *Angew. Chem., Int. Ed.* **2023**, *62*, e202310812. (d) Fa, S.; Adachi, K.; Nagata, Y.; Egami, K.; Kato, K.; Ogoshi, T. Pre-Regulation of the Planar Chirality of Pillar[5]arenes for Preparing Discrete Chiral Nanotubes. *Chem. Sci.* **2021**, *12*, 3483–3488. (e) Wan, X.; Li, S.; Tian, Y.; Xu, J.; Shen, L.-C.; Zuilhof, H.; Zhang, M.; Sue, A. C.-H. Twisted Pentagonal Prisms: Ag_nL₂ Metal-organic Pillars. *Chem* **2022**, *8*, 2136–2147. (f) Kato, K.; Ohtani, S.; Fa, S.; Ogoshi, T. Discrete and Continuous One-Dimensional Channels Based on Pillar[*n*]arenes. *Bull. Chem. Soc. Jpn.* **2021**, *94*, 2319–2328. (15) Fa, S.; Shi, T.-H.; Akama, S.; Adachi, K.; Wada, K.; Tanaka, S.; Oyama, N.; Kato, K.; Ohtani, S.; Nagata, Y.; Akine, S.; Ogoshi, T. Real-time Chirality Transfer Monitoring from Statistically Random to Discrete Homochiral Nanotubes. *Nat. Commun.* **2022**, *13*, 7378. (16) (a) Zafrani, Y.; Kaizerman, D.; Hadar, M.; Bigan, N.; Granot, E.; Ghosh, M.; Adler-Abramovich, L.; Patolsky, F.; Cohen, Y. Pillararene-Based Two-Component Thixotropic Supramolecular Organogels: Complementarity and Multivalency as Prominent Motifs. *Chem. – Eur. J.* **2018**, *24*, 15750–15755. (b) Kaizerman-Kane, D.; Hadar, M.; Granot, E.; Patolsky, F.; Zafrani, Y.; Cohen, Y. Shape Induced Sorting via Rim-to-rim Complementarity in the Formation of Pillar[5, 6]arene-based Supramolecular Organogels. *Org. Chem. Front.* **2019**, *6*, 3348–3354. (17) (a) Ogoshi, T.; Takashima, S.; Yamagishi, T. Molecular Recognition with Microporous Multilayer Films Prepared by Layer-by-Layer Assembly of Pillar[5]arenes. *J. Am. Chem. Soc.* **2015**, *137*, 10962–10964. (b) Ogoshi, T.; Takashima, S.; Yamagishi, T. Photo-controlled Reversible Guest Uptake, Storage, and Release by Azobenzene-Modified Microporous Multilayer Films of Pillar[5]arenes. *J. Am. Chem. Soc.* **2018**, *140*, 1544–1548. (18) The non-rigid methylene bridges of pillar[5]arene allow the units to “swing” while maintaining the helical chirality. Such a “swing effect” makes the molecule not always perfectly pillar-shaped in solution, resulting in the CD intensity being not maximized. Guest inclusion and self-assembly can prohibit the molecule from swinging, which helps to increase the CD intensity. This phenomenon has been well explained in reference 15. (19) (a) Shu, X.; Fan, J.; Li, J.; Wang, X.; Chen, W.; Jia, X.; Li, C. Complexation of Neutral 1,4-Dihalobutanes with Simple Pillar[5]arenes that is Dominated by Dispersion Forces. *Org. Biomol. Chem.* **2012**, *10*, 3393–3397. (b) Shu, X.; Chen, S.; Li, J.; Chen, Z.; Weng, L.; Jia, X.; Li, C. Highly Effective Binding of Neutral Dinitriles by Simple Pillar[5]arenes. *Chem. Commun.* **2012**, *48*, 2967–2969. (20) The guest complexation and reduced units swing are supported by ¹H NMR titration and CD intensity enhancement after adding guest molecule into P5As monomers (Figures S17, S20 and S21). (21) (a) Babu, S. S.; Praveen, V. K.; Ajayaghosh, A. Functional π -Gels and Their Applications. *Chem. Rev.* **2014**, *114*, 1973–2129. (b) Yokoya, M.; Kimura, S.; Yamanaka, M. Urea Derivatives as Functional Molecules: Supramolecular Capsules, Supramolecular Polymers, Supramolecular Gels, Artificial Hosts, and Catalysts. *Chem. – Eur. J.* **2021**, *27*, 5601–5614. (22) (a) Xia, D.; Wang, P.; Ji, X.; Khashab, N. M.; Sessler, J. L.; Huang, F. Functional Supramolecular Polymeric Networks: The Marriage of Covalent Polymers and Macrocyclic-Based Host–Guest Interactions. *Chem. Rev.* **2020**, *120*, 6070–6123. (b) Peng, H.-Q.; Zhu, W.;

Guo, W.-J.; Li, Q.; Ma, S.; Bucher, C.; Liu, B.; Ji, X.; Huang, F.; Sessler, J. L. Supramolecular Polymers: Recent Advances Based on the Types of Underlying Interactions. *Prog. Polym. Sci.* **2023**, *137*, 101635.

- (23) (a) Kashiwagi, D.; Sim, S.; Niwa, T.; Taguchi, H.; Aida, T. Protein Nanotube Selectively Cleavable with DNA: Supramolecular Polymerization of “DNA-Appended Molecular Chaperones”. *J. Am. Chem. Soc.* **2018**, *140*, 26–29. (b) Kashiwagi, D.; Shen, H. K.; Sim, S.; Sano, K.; Ishida, Y.; Kimura, A.; Niwa, T.; Taguchi, H.; Aida, T. Molecularly Engineered “Janus GroEL”: Application to Supramolecular copolymerization with a Higher Level of Sequence Control. *J. Am. Chem. Soc.* **2020**, *142*, 13310–13315.



Supporting Information

Helical-Sense Matching Facilitates Supramolecular Copolymerization of Helical-chiral Pillar[5]arenes

De-Hui Tuo,^{1,2,†} Shixin Fa,^{3,†,*} Seigo Tanaka,² Takuma Shimada,⁴ Masataka Yamashita,⁵ Yuki Togari,² Shunsuke Ohtani,² Kenichi Kato,² Kenji Urayama,⁵ Qiuyu Zhang,³ Kazuma Yasuhara,⁶ Tomoki Ogoshi^{1,2,*}

¹WPI Nano Life Science Institute (WPI-NanoLSI), Kanazawa University, Kakuma-machi, Kanazawa, 920-1192, Japan

²Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto, 615-8510, Japan

³School of Chemistry and Chemical Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi, 710072, P. R. China

⁴Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, 615-8510, Japan

⁵Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto, 615-8510, Japan

⁶Division of Materials Science, Nara Institute of Science and Technology, Ikoma, Nara, 630-0192, Japan.

[†]These authors contributed equally.

*Correspondence to S.F.: sfa@nwpu.edu.cn and to T.O.: ogoshi.tomoki.3s@kyoto-u.ac.jp

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1. General information

All reagents and solvents were commercial reagents, which were used without further purification except where noted. ^1H (500 MHz) and ^{13}C (126 MHz) NMR spectra were recorded on a JEOL ECZ-500 spectrometer. Viscosity measurements were measured by KYOTO ELECTRONICS EMS-1000. High Resolution Electrospray Ionization Fourier Transform (HR-ESI-FT) mass spectra were recorded on a Thermo Fisher Scientific EXACTIVE Plus instrument by using the ESI method in positive ion mode. Ultraviolet/visible (UV-Vis) absorption spectra were measured on a JASCO V-750 spectrometer, circular dichroism (CD) spectra were measured by JASCO J-1500 and 2 mm quartz cuvettes were used. HPLC separation of P5A **3** was conducted on a Japan Analytical Industry LaboACE LC-5060 recycling HPLC apparatus equipped with a DAICEL CHIRALPAK IA (Φ = 20 mm, l = 250 mm), and chiral fractions were analyzed with a Hitachi High-Performance Liquid Chromatograph Chromaster instrument equipped with a DAICEL CHIRALPAK IA (Φ = 4.6 mm, l = 250 mm) column. Atomic force microscopy (AFM) was performed on a Bruker, model Multi Mode 8 atomic force microscope under ambient conditions in the scan assist mode. AFM images were analyzed by Bruker, Nanoanalysis. Scanning electron microscope (SEM) images were acquired with HITACHI SU8220 FE-SEM at accelerating voltages of 5.0 kV. The TEM observation was performed using JEM-3100FEF (JEOL Ltd., Tokyo, Japan) at an acceleration voltage of 300 kV. The microscopic image was recorded using an ORIUS SC-200 camera installed in the microscope. Particle size distribution was measured on a DLS instrument (Malvern Zetasizer μV) equipped with 830 nm diode laser as a light source, using a fixed angle (90°) at room temperature. Rheological measurements were performed using a Modular Compact Rheometer MCR 502 (Anton Paar, Graz, Austria).

2. Synthetic procedure and optical resolution

Peramino-P5A **2** was synthesized and optically separated following the previous report.^{S1} Ester-P5A **3** was synthesized following the reported synthetic routine,^{S2} and optically separated by HPLC. The optical resolution of **3** was conducted with chiral HPLC (Figure S1). The reinjections to chiral HPLC confirm that both fractions are optically pure (1st fraction: e.e. > 99.5%, 2nd fraction: e.e. > 99.5%).

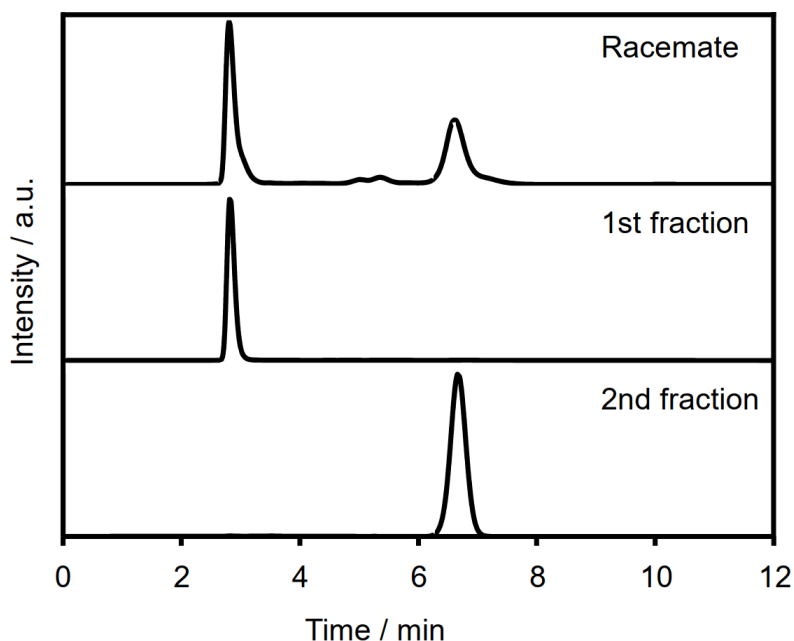
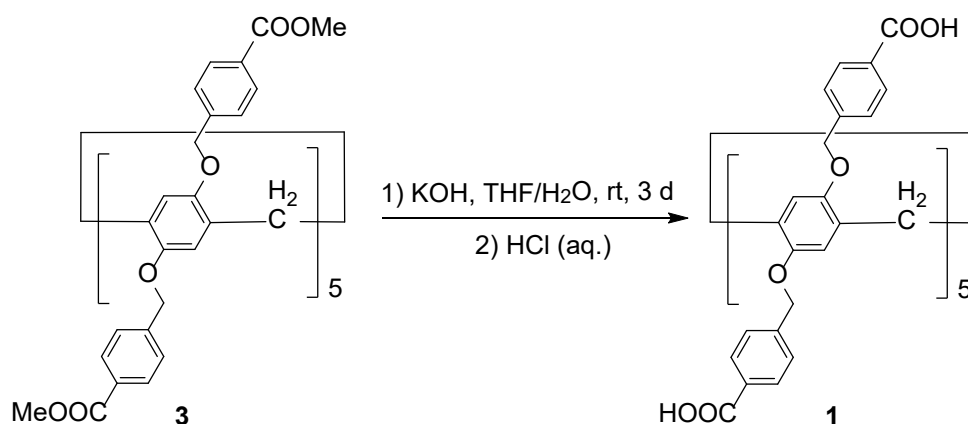


Figure S1. Chiral HPLC traces (*n*-hexane/dichloromethane, 1/4, v/v, 25 °C) of *rac*-**3** and the re-injected first (*M*-**3**) and second (*P*-**3**) fractions. Column: DAICEL CHIRALPAK® IA (Φ = 4.6 mm, *l* = 250 mm).

The optical resolution of peracid-P5A **1** is difficult due to the ten polar benzoic acids on the structure. Enantiomeric peracid-P5A **1** was obtained by hydrolysis of the separated *M*-**3** and *P*-**3** at room temperature following the previous reported condition (Scheme S1).^{S2}



Scheme S1. Synthesis of enantiomeric peracid-P5A **1**.

M-1: Enantiomeric **M-3** (71 mg, 0.034 mmol) obtained by HPLC separation was dissolved in THF (12 mL), and KOH (aq.) (12 mL, 0.28 M) was poured into the solution with cooling in an ice bath. The resulting solution was stirred at room temperature for 3 days. After evaporating THF under reduced pressure, the obtained aqueous solution was acidified with HCl (aq.) until pH equal to 1. The product was filtered, washed with CHCl₃ and vacuum-dried to afford **M-1** as a yellow solid (57 mg, 86%).

¹H NMR (500 MHz, *d*₆-DMSO, 298 K): δ (ppm) = 7.96 (d, *J* = 8 Hz, 20H), 7.46 (d, *J* = 8.5 Hz, 20H), 6.88 (s, 10H), 4.68 (dd, *J* = 44, 12 Hz, 20H), 3.82 (s, 10H); HR ESI-FT-MS (positive): *m/z* calcd for 1950.5517 [C₁₁₅H₉₀O₃₀]⁺: 1973.5409 [M+Na]⁺; found: 1973.5477.

P-1 (85%): Synthesized in the same way as **M-1**. The characterization data are consistent. The CD spectra of **M-1** and **P-1** present mirror images (Figure S3).

3. Sample preparation and characterization

The chiral supramolecular copolymerization was investigated through three different combinations of **1** and **2**: the combination of the same chiral fractions (e.g., *M-1* and *M-2*), i.e. **homo**; the combination of opposite chiral fractions (e.g., *M-1* and *P-2*), i.e. **hetero**; and the combination of racemic **1** and **2**, named **racemate**. Due to solubility issue of **1**, the supramolecular co-assembly was conducted by mixing combined solvents of **1** in DMSO and an equivalent concentration of **2** in chloroform at a ratio of 1:1 (v/v).

The DMSO solution of **1** (0.80 mM) and chloroform solution of **2** (0.80 mM) were prepared separately. The two samples were kept at 30 °C in a water bath, and then 300 μ L of each solution was mixed in a 2 mL vial and sonicated for 1 min. It turned out to be gel for **homo**, while **hetero** and **racemate** resulted in turbid and clear solvent respectively. In case of time dependencies for the **homo** gel, characterization was conducted after 24 h.

The gel-to-sol transition temperature (T_{gel}) of **homo** gel was conducted within a 2 mL vial. The gel was heated at a rate under 1 °C/min in oil bath, the temperature at which gel deformed and became solution was determined as T_{gel} .^{S3} The experiment was repeated several times for confirmation (58 ± 1 °C for 0.40 mM DMSO/Chloroform **homo** gel).

4. Investigation of solvent effects

Solvents show significant effects on supramolecular copolymerization. Due to solubility issue of **1**, the supramolecular copolymerization was conducted by mixing combined solvents of **1** in DMSO and **2** in other solvents. As shown in Table S1, the DMSO/CHCl₃ system was the only case among the measured solvent systems that gave gel formation of the **homo** combination. Other solvent systems, such as DMSO/THF, DMSO/Acetone and DMSO/Toluene, only precipitate or transparent solvent was observed for all the combinations.

Table S1. Solvent effects on gel formation

Solvent (1/1, v/v)	Homo	Hetero	Racemate
DMSO/Chloroform	Gel (58 °C)	Sol	Sol
DMSO/THF	Sol	Sol	Precipitate
DMSO/Toluene	Precipitate	Sol	Precipitate
DMSO/Acetone	Sol	Sol	Precipitate

The concentration for each monomer is 0.40 mM, parenthesis: Gel-to-sol transition temperature.

5. DLS results

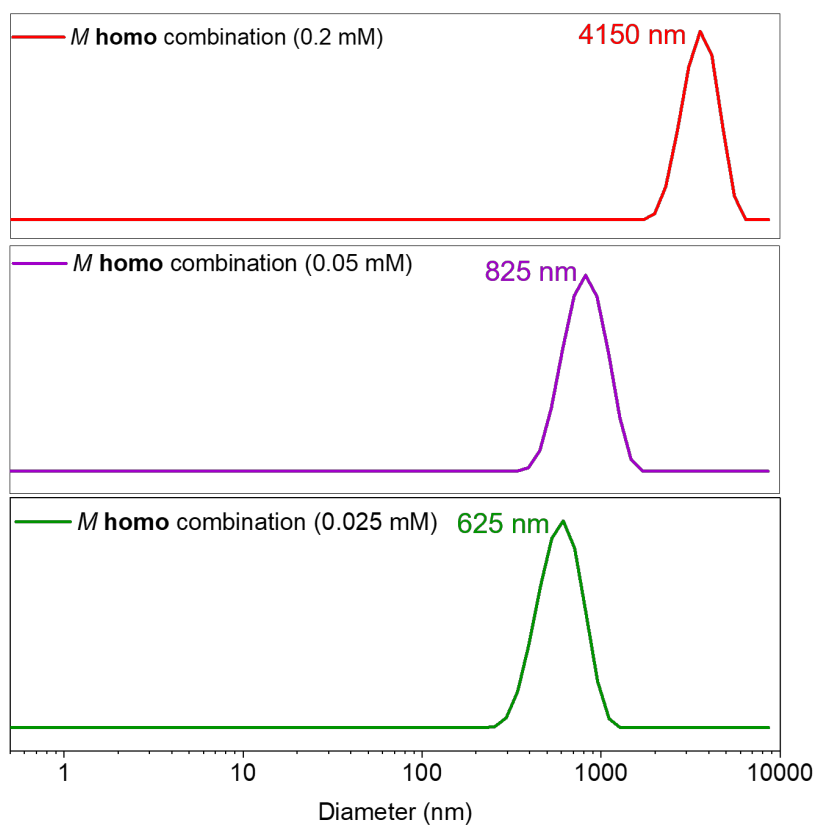


Figure S2. Size distributions of the **homo** combination by increasing the concentrations from 0.025 mM to 0.2 mM. The diameters gradually changed from 625 nm to 4150 nm by increasing the concentrations.

6. Rheological results

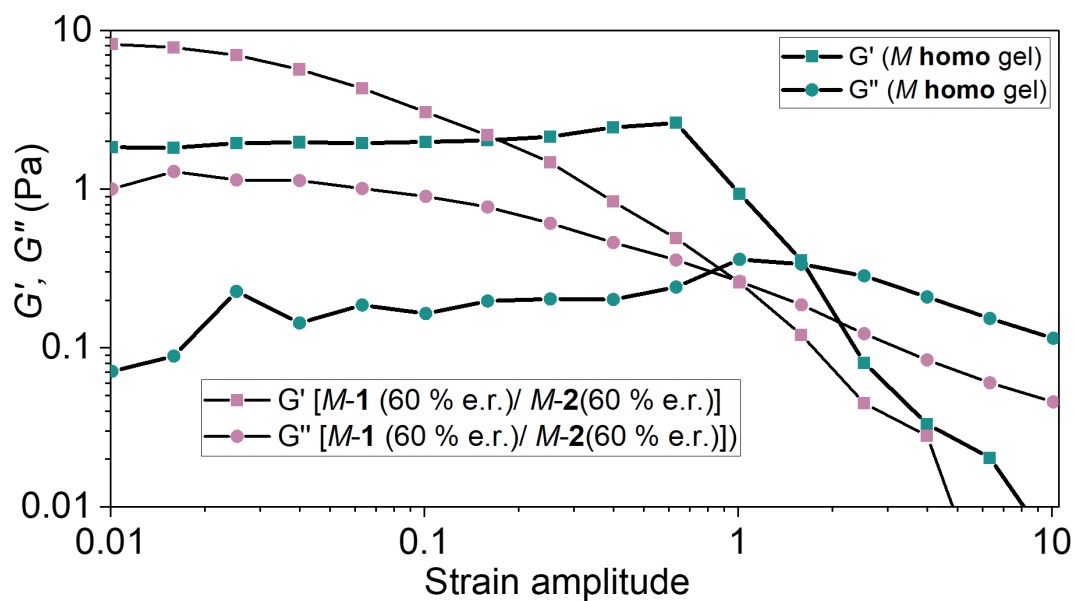


Figure S3. The storage (G') and loss (G'') moduli as a function of strain amplitude at a frequency of 1.0 Hz for *M homo* gel and *M-1*(60 % e.r.)/*M-2*(60 % e.r.) composed gel (Chloroform: DMSO = 1:1 v/v, each monomer: 0.40 mM, 25 °C).

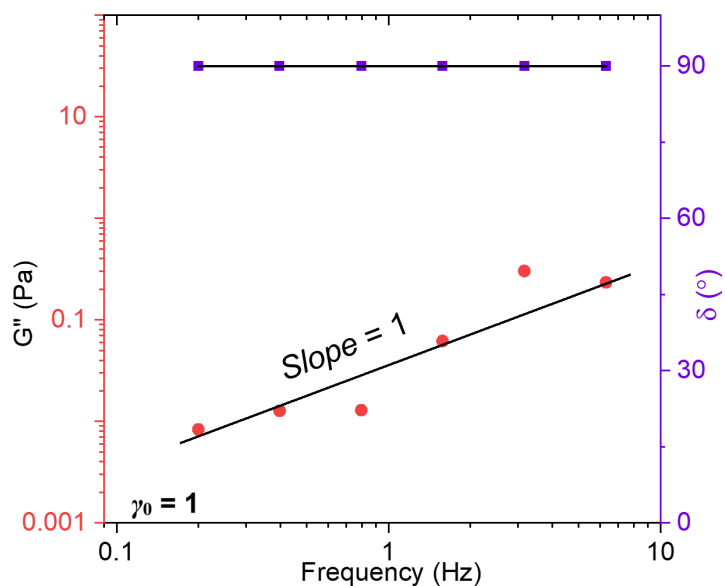


Figure S4. Loss shear modulus (G'' , red circles) and phase angle (δ , purple squares) as a function of frequency of **hetero** (*M-1* and *P-2*) combinations (Chloroform: DMSO = 1:1 v/v, each monomer: 0.40 mM, 25 °C). The applied strain amplitude was within linear response regime.

7. CD and UV-Vis spectra

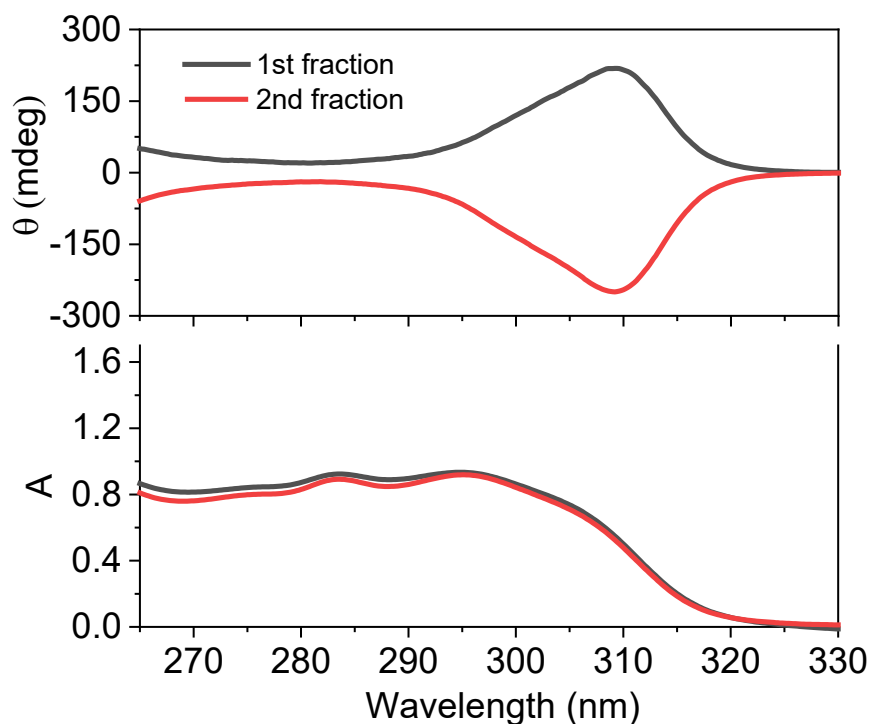


Figure S5. CD and UV-Vis spectra of **3** (CHCl_3 , 0.40 mM, 25 °C) after HPLC separation.

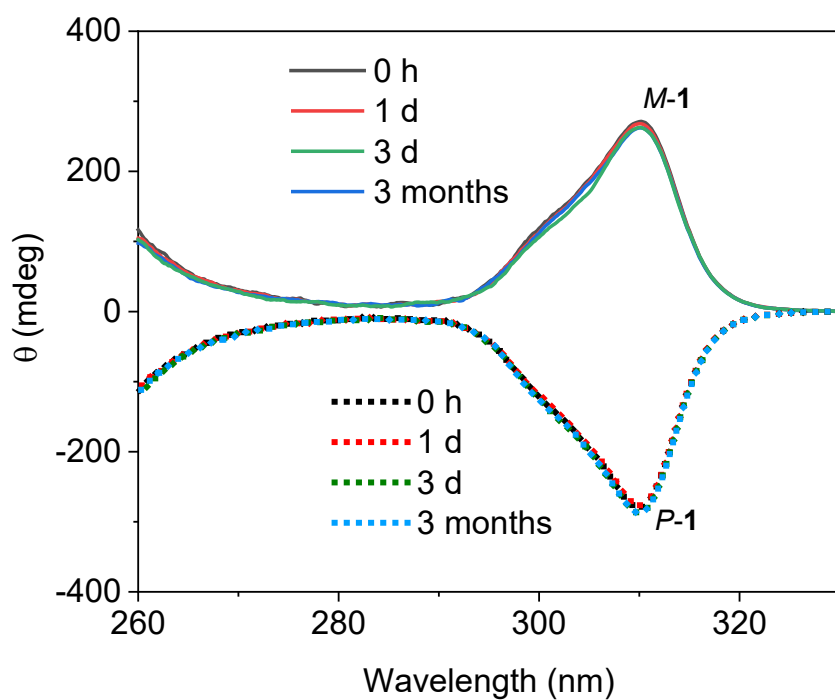


Figure S6. CD spectra of **1** (Chloroform: DMSO = 1:1 v/v, 0.40 mM, 25 °C). Both chiral fractions were retained at room temperature for over 3 months.

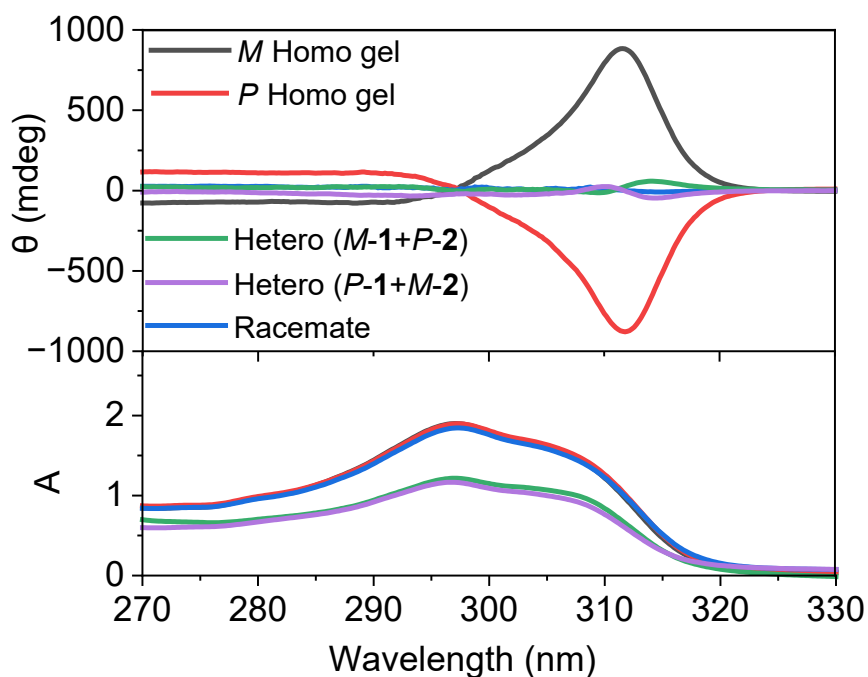


Figure S7. CD and UV-Vis spectra of **homo**, **hetero** and **racemate** (Chloroform: DMSO = 1:1 v/v, each monomer: 0.40 mM, 25 °C). The UV-Vis spectra of **homo** and **racemate** are consistent, which are different from the **hetero**, indicating self-sorted, helical-sense-matched assembly behavior in the **racemate**.

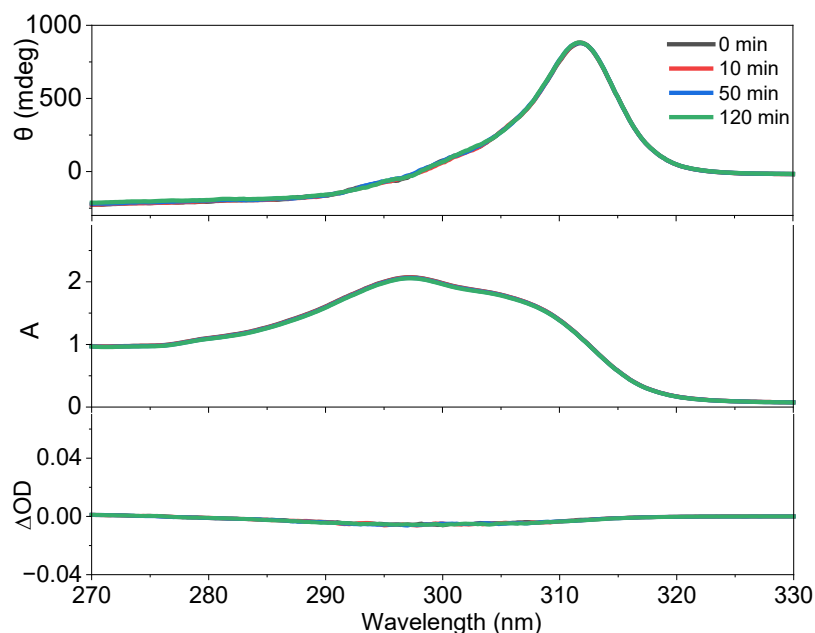


Figure S8. Time dependent CD and UV-Vis spectra for **M homo gel** (Chloroform: DMSO = 1:1 v/v, each monomer: 0.40 mM, 25 °C) formation, the weak linear dichroism (LD) signals indicate homogeneous assembled structures.

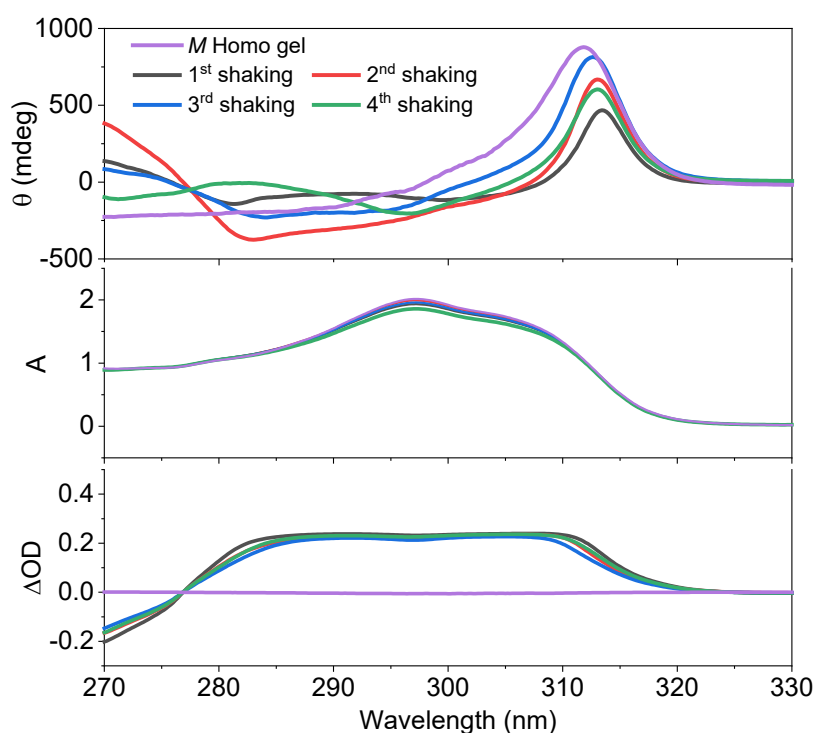


Figure S9. Spectral changes towards shaking of the *M homo* gel (Chloroform: DMSO = 1:1 v/v, each monomer: 0.40 mM, 25 °C). The obvious linear LD signals were attributed to inhomogeneous assembled structure formation after shaking.

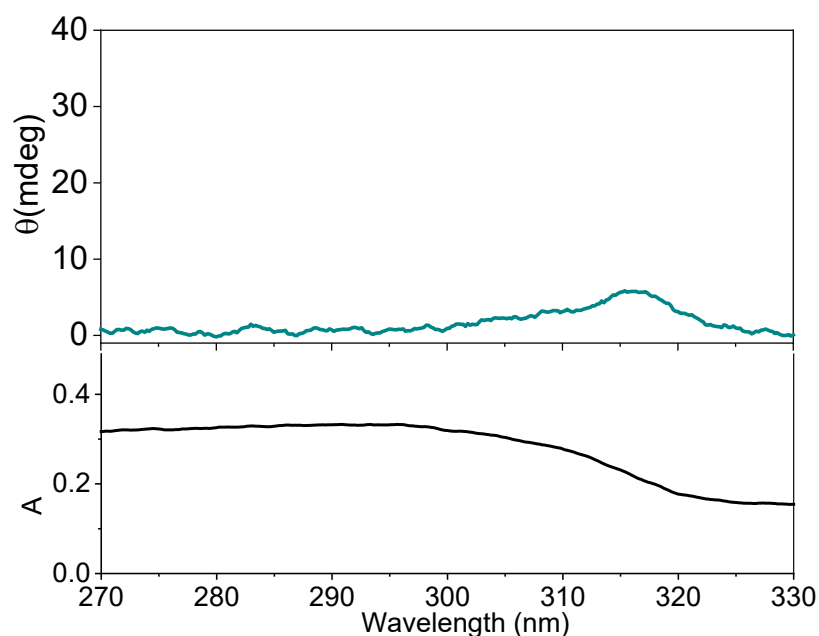


Figure S10. CD and UV-Vis spectra of the turbid solvent from *M homo* gel transformation by keeping the **homo** gel at around 30 °C for several days. (Chloroform: DMSO = 1:1 v/v, each monomer: 0.40 mM).

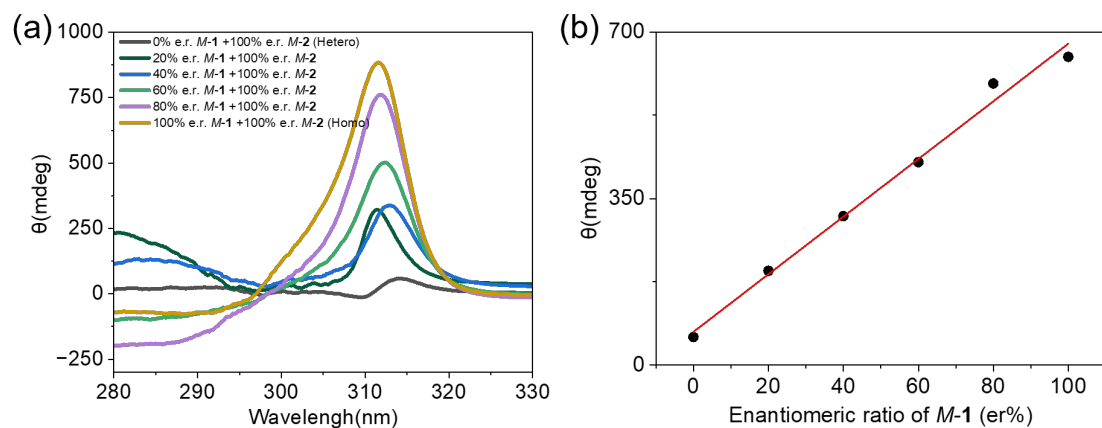


Figure S11. CD spectral changes upon the e.r. value changes of *M*-1 in *M* homo combination (a) and the CD intensity change (314 nm) with the e.r. value of *M*-1 (b).

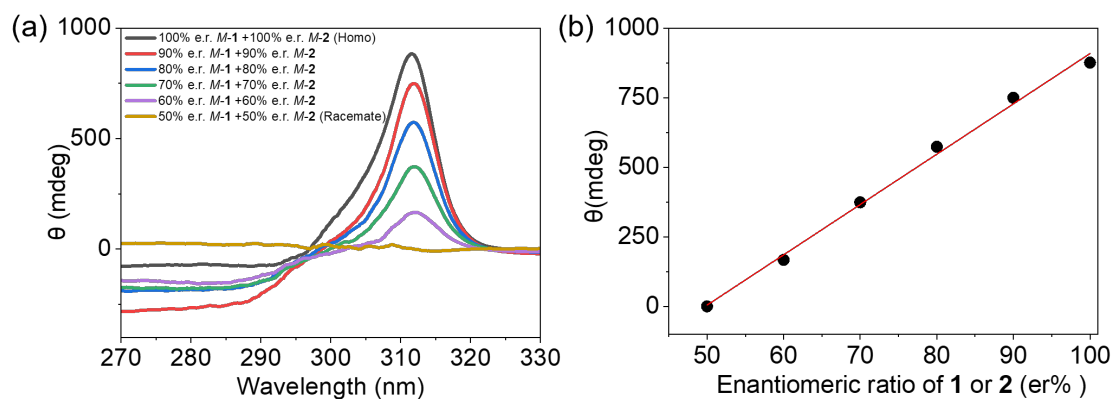


Figure S12. CD spectral changes upon the e.r. values change of *M*-1 and *M*-2 simultaneously (a), and the CD intensity (314 nm) change with the e.r. value of *M*-1 or 2 (b).

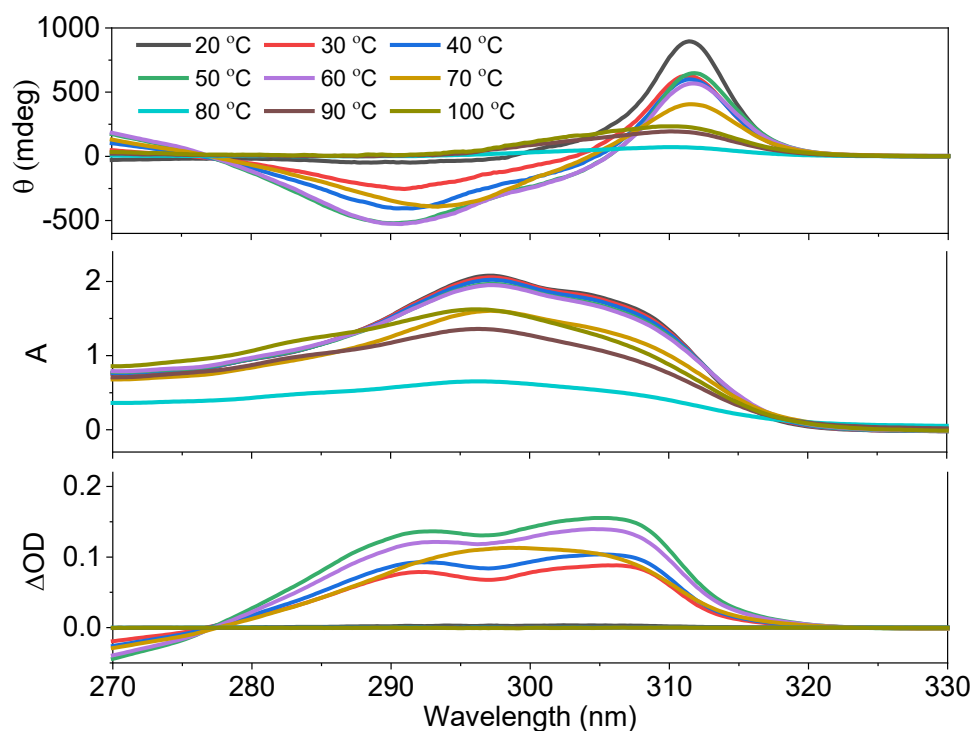


Figure S13. Temperature-dependent spectral changes of *M homo* gel (Chloroform: DMSO = 1:1 v/v, each monomer: 0.40 mM). The CD spectra exhibit significant fluctuations with continuous temperature increase. CD intensity at 312 nm reached its minimum value at 80 °C because the transformed nanoparticles completely precipitated out. By further increasing temperature from 80 °C to 100 °C, the CD intensity slightly increased because nanoparticle began to dissolve and the sample transformed into clear solvent. The obvious LD signals were attributed to inhomogeneous assembled structure formation.

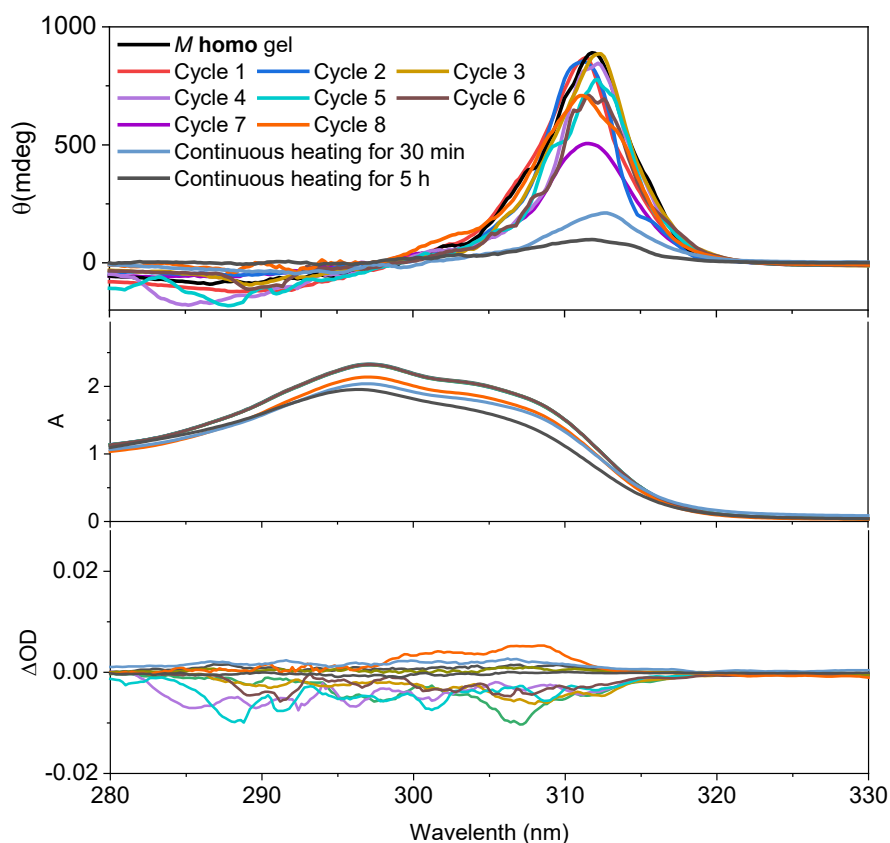


Figure S14. Spectral changes for *M homo* gel recovery (chloroform: DMSO = 1:1 v/v, each monomer: 0.40 mM) by standing the sample at 100 °C for 1 min and then quickly immersing in ice water for 1 min. This process can be repeated at least for eight times until racemization occurs by continuous heating. The fluctuated spectra were attributed to LD signals.

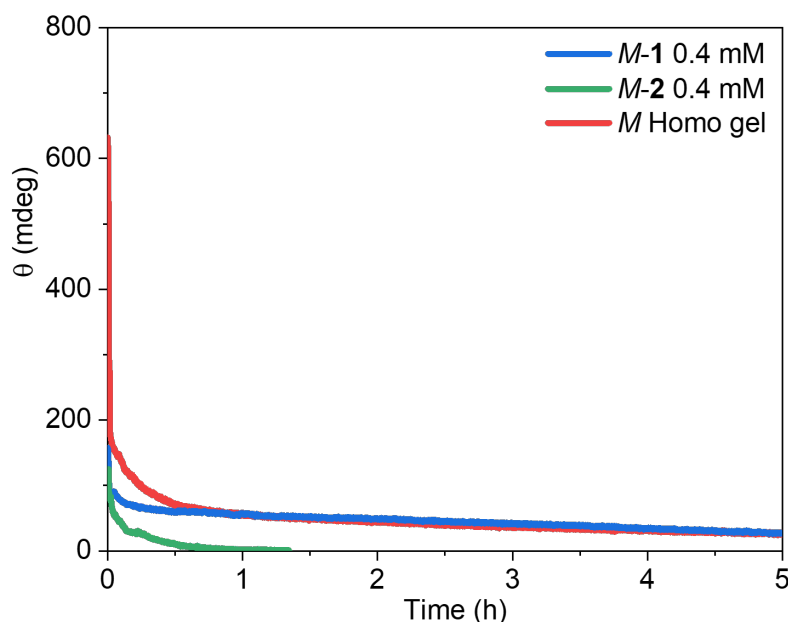


Figure S15. Time-dependent CD intensity changes of monomer *M-1*, *M-2* and *M homo* gel samples at 100 °C (Chloroform: DMSO = 1:1 v/v, each monomer: 0.40 mM, recorded at 312 nm). CD intensity of *M-1* in blue line shows sharp decreased CD intensity at the initial stage and then decrease slowly with time because of racemization. CD intensity of *M-2* in green line sharply decreases at 100 °C and becomes **racemate** within one hour. The intensity of *M homo* gel in red line shows obvious decrease within one hour because of the fast racemization of *M-2*, and then slowly decrease because of the gradual racemization of *M-1*. The sharply decreased CD intensities at the initial stage for all the samples were attributed to the violet swing of the P5A units at 100 °C in solution.^{S4}

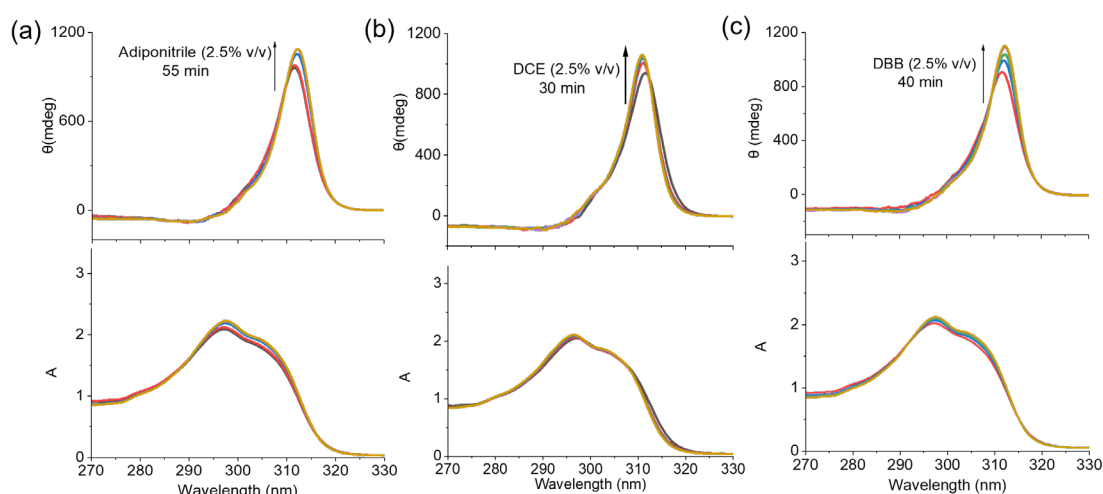


Figure S16. CD (top) and UV-Vis (bottom) spectral changes of the *M homo* gel upon addition of adiponitrile (2.5% v/v) (a), DCE (2.5% v/v) (b) and DBB (2.5% v/v) (c). The time-dependent CD intensity changes were attributed to diffusion of guest molecules in the gel sample.

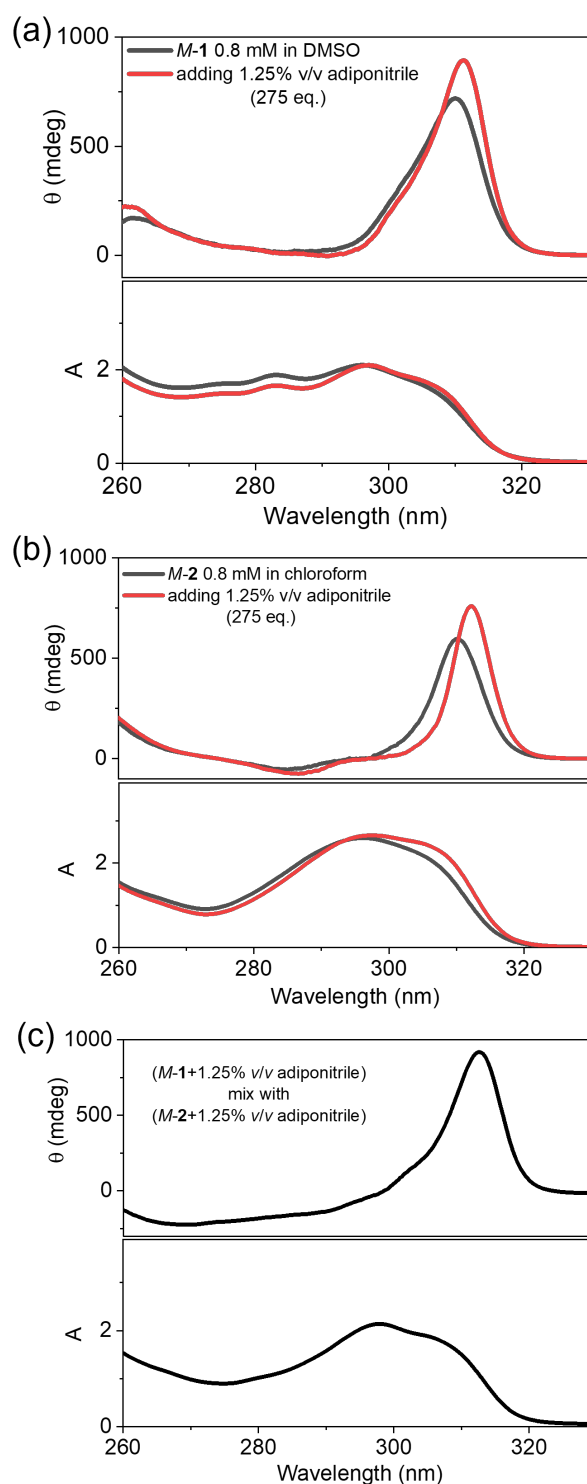


Figure S17. CD and UV-Vis spectral changes of monomers upon addition of (a) adiponitrile (2.5% v/v, 275 eq.) into *M-1* (0.8 mM, DMSO) and (b) *M-2* (0.8 mM, chloroform). (c) CD and UV-Vis spectra of the **homo** gel (chloroform: DMSO = 1:1 v/v, each monomer: 0.40 mM) formed by mixing DMSO solution of *M-1* (0.8 mM) with adiponitrile (275 eq.) and chloroform solution of *M-2* (0.8 mM) with adiponitrile (275 eq.).

8. Transformation of the homo gel

The transformation of the **homo** gel (nanowire) to turbid solution (nanoparticle) was initially investigated by Eyring equation. The **homo** gel samples (Chloroform: DMSO = 1:1 v/v, each monomer: 0.40 mM) in a 2 mm quartz cuvette were heated to 50 °C, 55 °C, 60 °C and 65 °C separately. The transmittance intensities of the samples at 296 nm were recorded. Considering the plateau at the initial stage where the transmittance intensity shows almost no change, the curves selected in Figure 4b are within the following ranges: 2 min to 1295 min at 50 °C, 5 min to 1333 min at 55 °C, 20 min to 1260 min at 60 °C, and 60 min to 1396 min at 65 °C. The thermodynamic parameters such as $\Delta H^\ddagger$, $\Delta S^\ddagger$ were determined from the slope and intercept by plotting $\ln(hk/k_B T)$ vs $1/T$ by using the linear Eyring plots^{S5}:

$$\ln \frac{hk}{k_B T} = -\frac{\Delta H^\ddagger}{R} \frac{1}{T} + \frac{\Delta S^\ddagger}{R}$$

where h , k_B and R are Planck constant, Boltzmann constant and molar gas constant, respectively. k is the reaction rate constant. By using the above equation, we speculated the transformation of the **homo** gel as a pseudo-first order reaction. $\Delta G^\ddagger$ was obtained according to the following equation:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

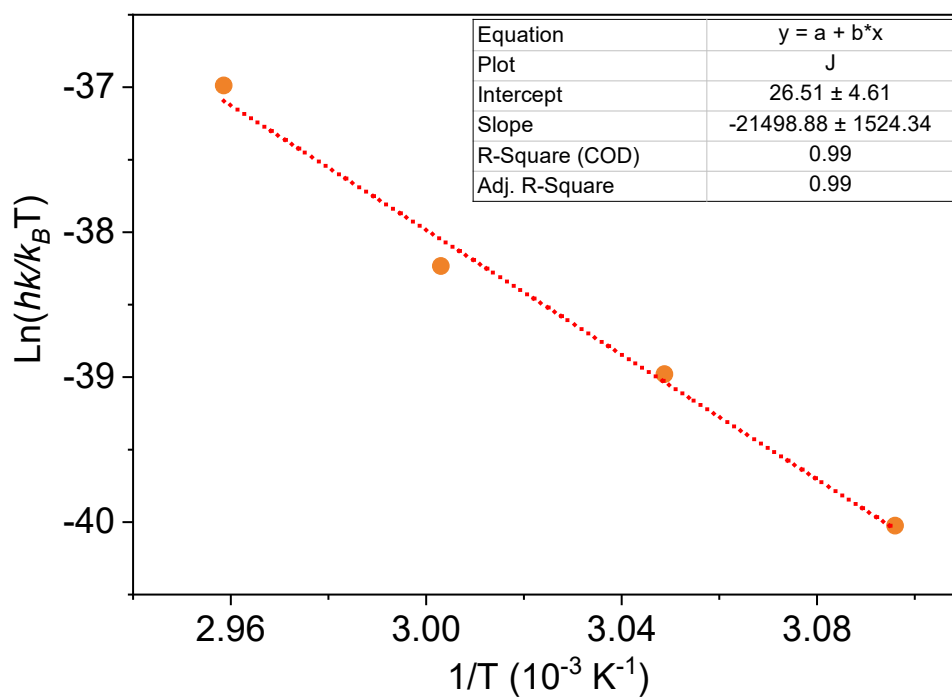


Figure S18. Eyring plots from the light transmittance changes of *M homo* gel at 296 nm. The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were determined to be 178.74 ± 12.67 kJ/mol, and 220.42 ± 38.33 J/mol/K, respectively. Therefore, the Gibbs energy of activation at 25 °C was determined to be $\Delta G_{\ddagger 25^\circ\text{C}} = 113.06 \pm 24.09$ kJ/mol.

9. ^1H NMR spectra

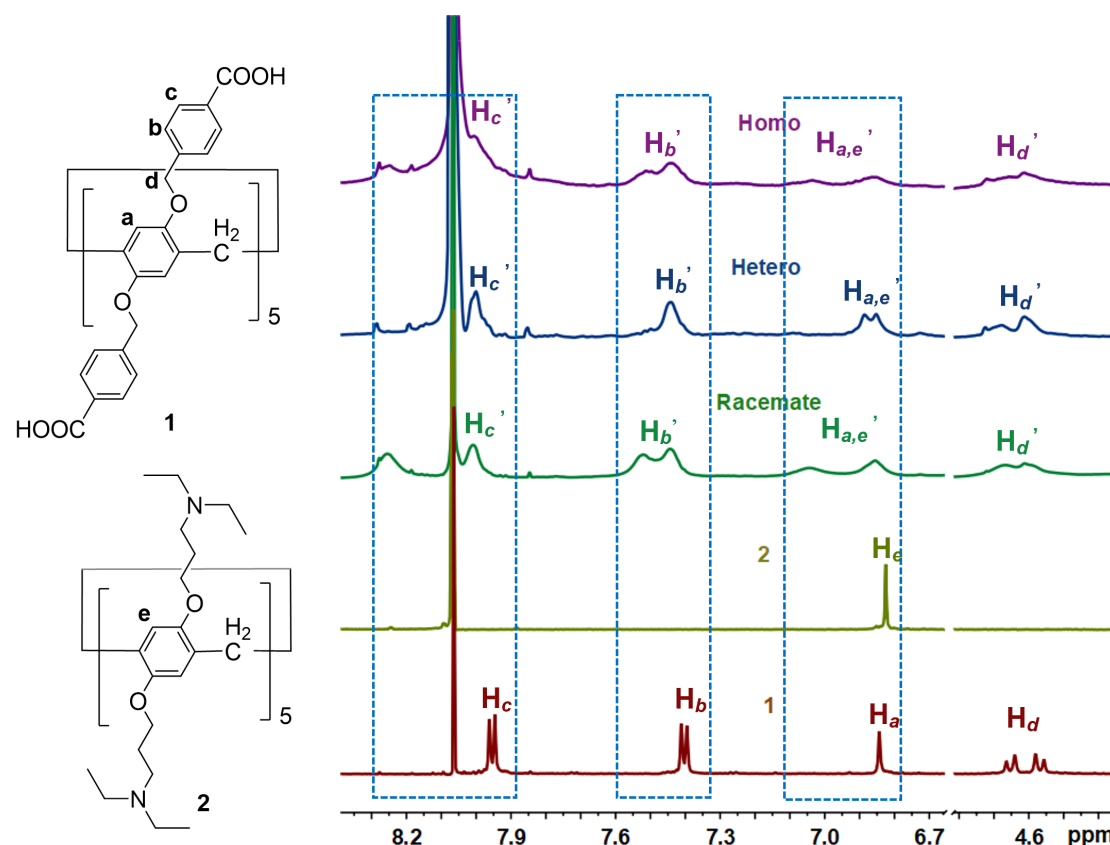


Figure S19. ^1H NMR spectra of **homo**, **hetero** and **racemate** combinations (CDCl_3 : $\text{DMSO}-d_6 = 1/1$ v/v, each monomer: 0.40 mM, 25 °C). The methene protons (H_{d}) on the two rims of **1** exhibit a distinct AB quartet split, indicating the bulky substituents hindered free rotation of P5A units and the chirality can be fixed. All the combinations presented broad and weak proton signals because of supramolecular copolymer formation. Meanwhile, different proton signals, like H_{b}' and H_{c}' , were observed in **homo** and **hetero**, attributing to homochiral match and heterochiral mismatch generated diastereoisomeric structures, while **homo** and **racemate** are almost consistent, indicating self-sorted, helical-sense-matched assembly behavior in **racemate**.

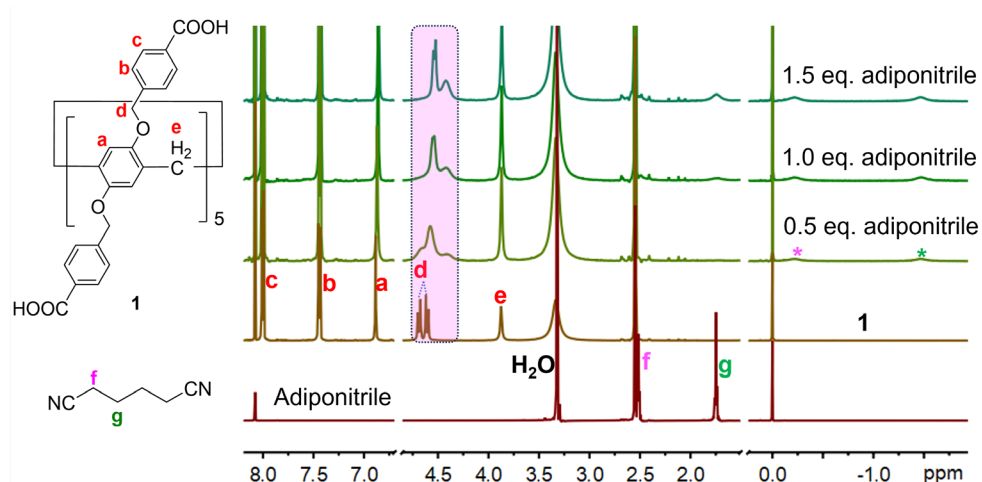


Figure S20. ^1H NMR titration by adding adiponitrile into the solution of **1** (CDCl_3 : $\text{DMSO-}d_6 = 1/1$ v/v, 5 mM). The distinct new proton signals (below zero) of adiponitrile (marked with asterisks) suggests slow formation of a complex on the NMR timescale. Based on the integration of the complexed and free proton signals of adiponitrile (1.0 eq.), the binding constant was determined to be $770 \pm 63 \text{ M}^{-1}$.

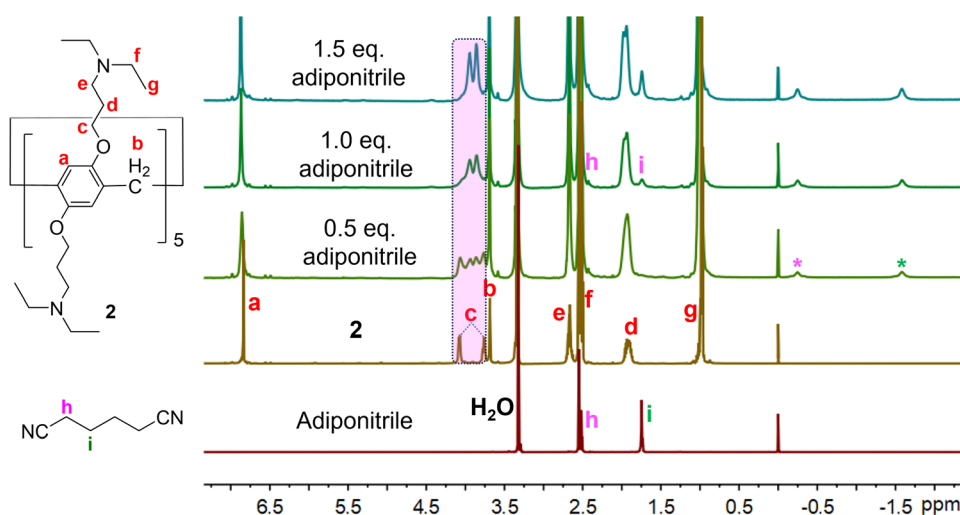


Figure S21. ^1H NMR titration by adding adiponitrile into the solution of **2** (CDCl_3 : $\text{DMSO-}d_6 = 1/1$ v/v, 5 mM). The distinct new proton signals (below zero) of adiponitrile (marked with asterisks) suggests slow formation of a complex on the NMR timescale. Based on the integration of the complexed and free proton signals of adiponitrile (1.0 eq.), the binding constant was determined to be $387 \pm 47 \text{ M}^{-1}$.

10. Images of electron microscopy

AFM measurements were carried out with the samples spread on highly oriented pyrolytic graphite (HOPG) plates with spin-coating method. TEM measurements were carried out with the sample solution placed on a grid mesh (Cu 200, JEOL, 780111621). SEM measurements were conducted on samples spread on ITO glass, followed by vacuum drying to rapidly remove the solvent.

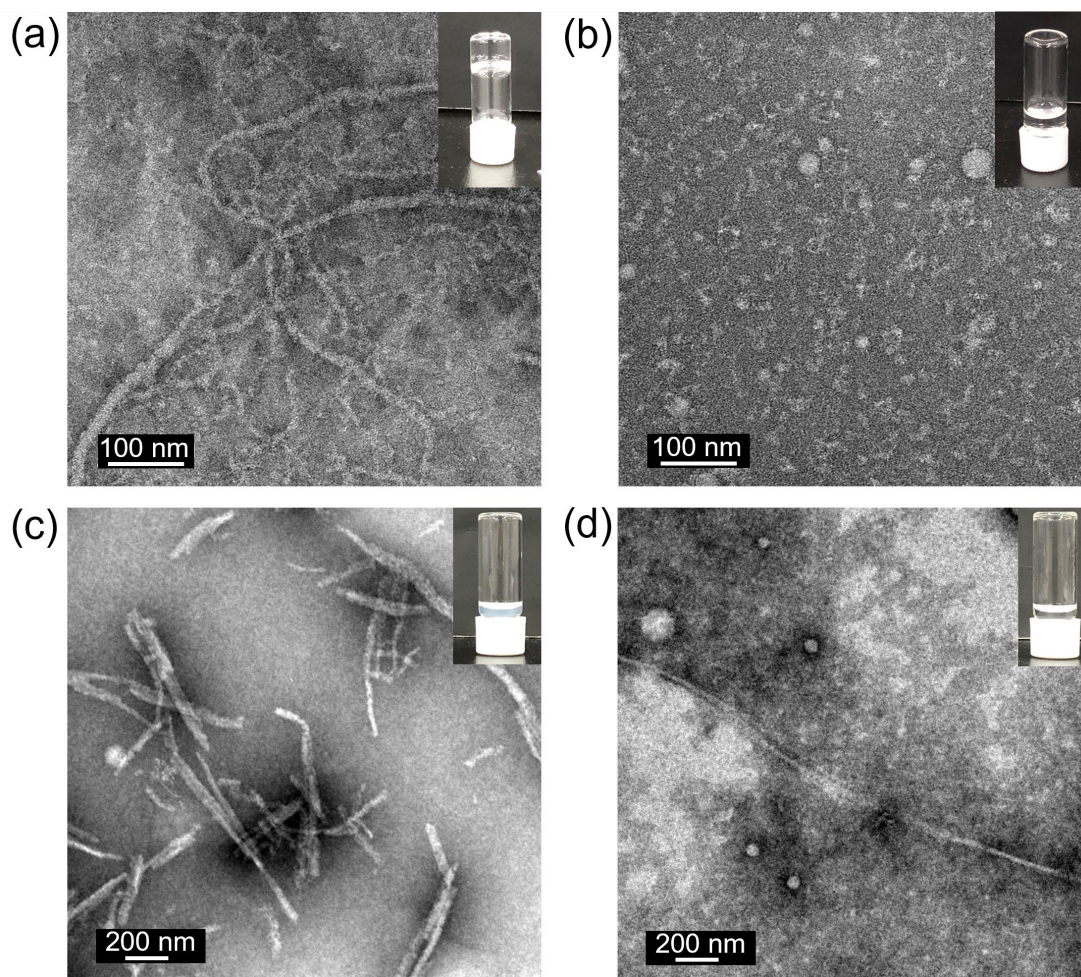


Figure S22. TEM images of each combination for **homo** gel (a), **homo** gel after shaking (b), **hetero** (c) and **racemate** (d) (CHCl_3 : DMSO = 1/1 v/v, each monomer: 0.40 mM, 25 °C). Inserted images show their physical properties.

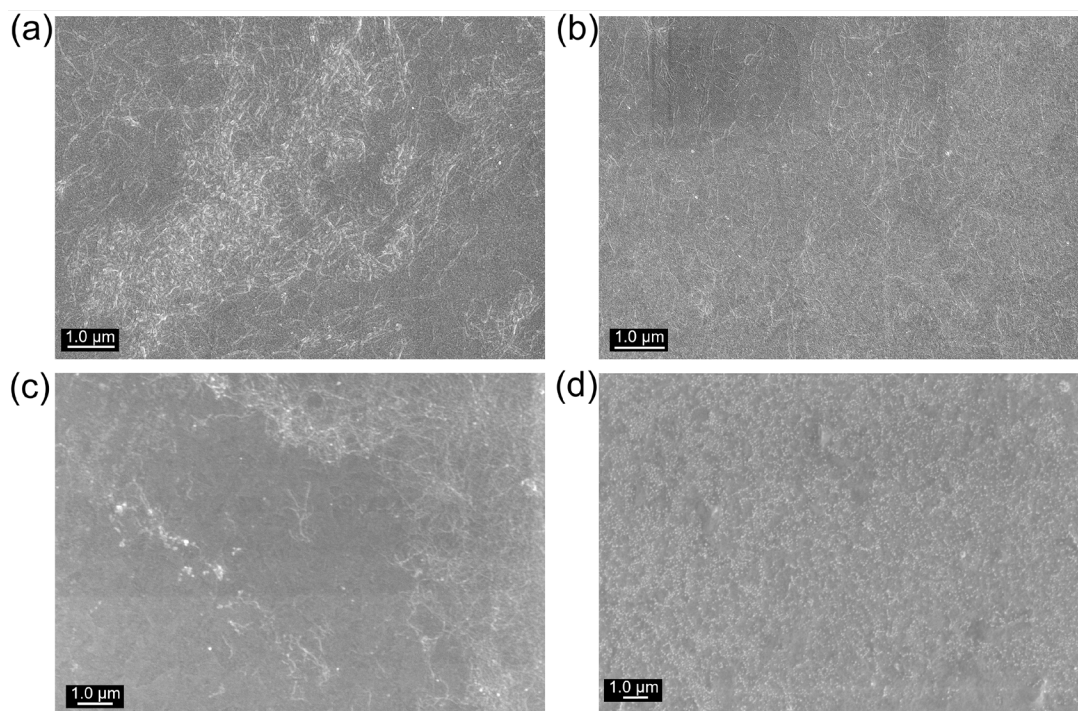


Figure S23. SEM images of **homo** solutions at the concentration of 0.1 mM (a), 0.05 mM (b) and 0.025 mM (CHCl₃: DMSO = 1/1 v/v, 25 °C) (c). Nanowires in the **homo** combination (0.05 mM) transforms into nanoparticles by heating at 60 °C for 2 hours (d).

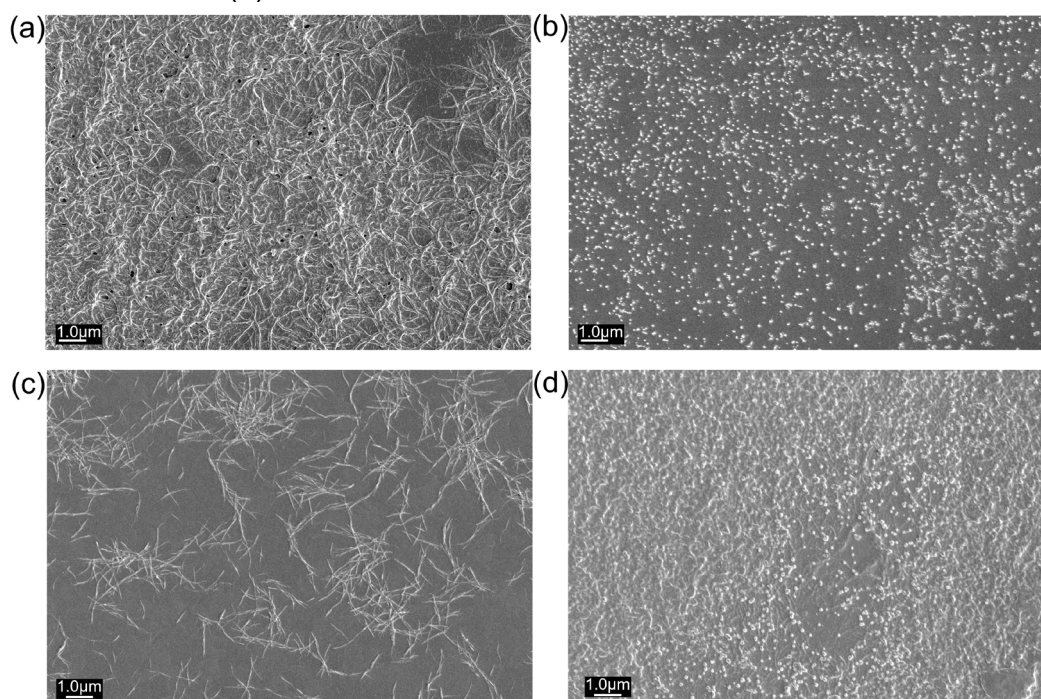


Figure S24. SEM images of each combination for **homo** gel (a), **homo** gel transforms into turbid solvent under the temperature over 30 °C for several days (b), **hetero** (c) and **racemate** (d). For the sake of obtaining clear microscopy images, the gel samples were diluted for the measurements (Chloroform: DMSO = 1:1 v/v, each monomer: 0.2 mM).

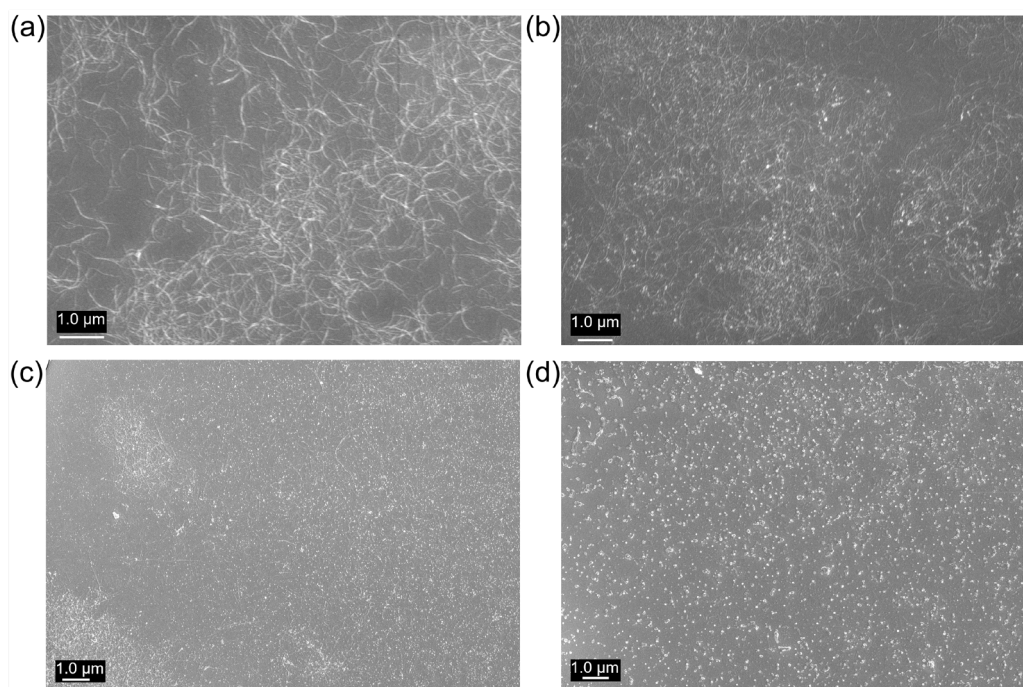


Figure S25. SEM monitoring of **homo** gel transformation at 40 °C for 0 h (a), 1 h (b), 2 h (c) and 6 h (d). For the sake of obtaining clear microscopy images, the gel samples were diluted for the measurements (Chloroform: DMSO = 1:1 v/v, each monomer: 0.2 mM).

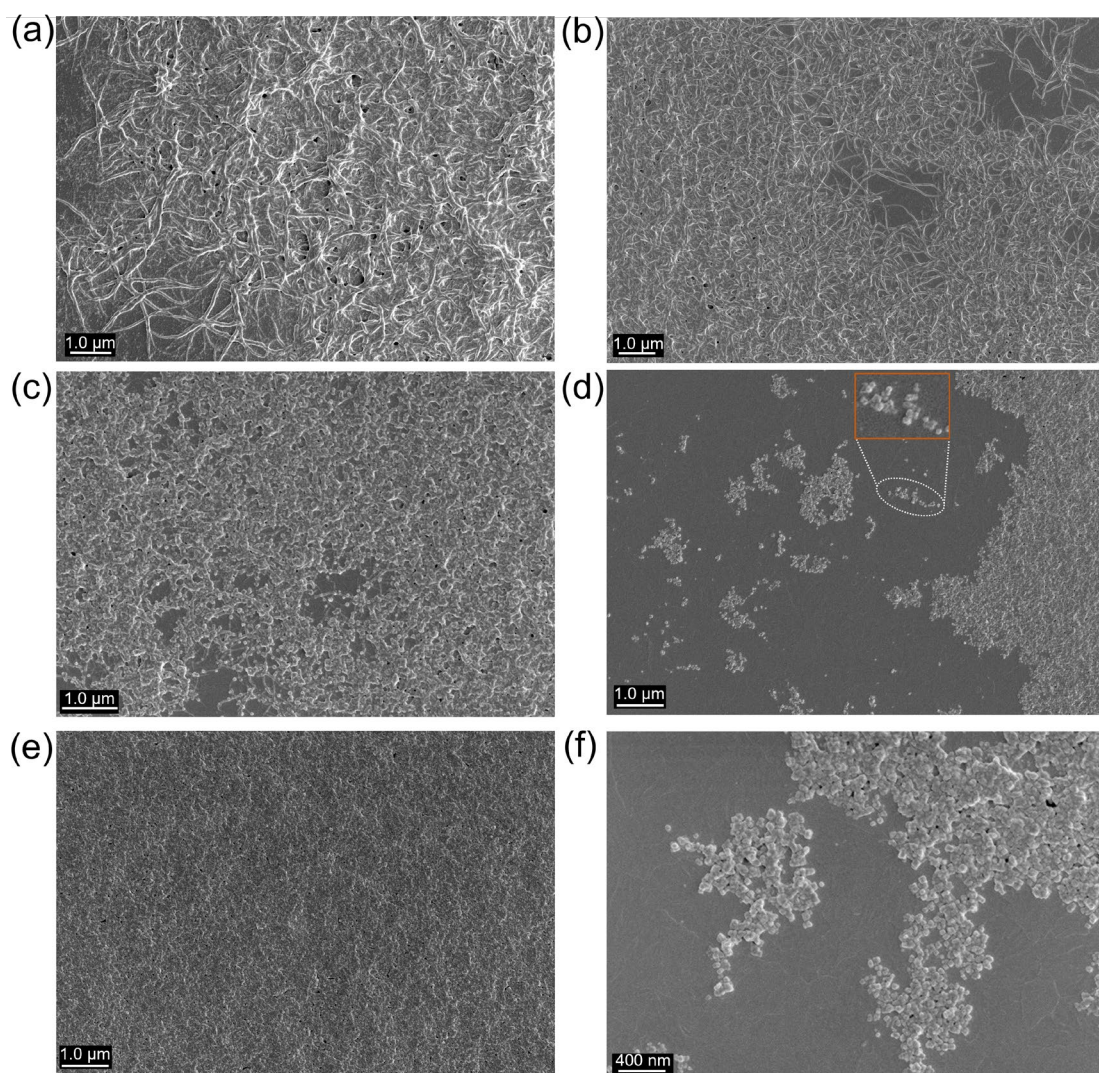


Figure S26. SEM images by changing the e.r. values of *M-1* in *M-1/M-2* combination, 100%/100% (i.e. **homo**) (a), 80%/100% (b), 60%/100% (c), 40%/100% (d) and 20%/100% (e, f). The concentration of each monomer is 0.2 mM.

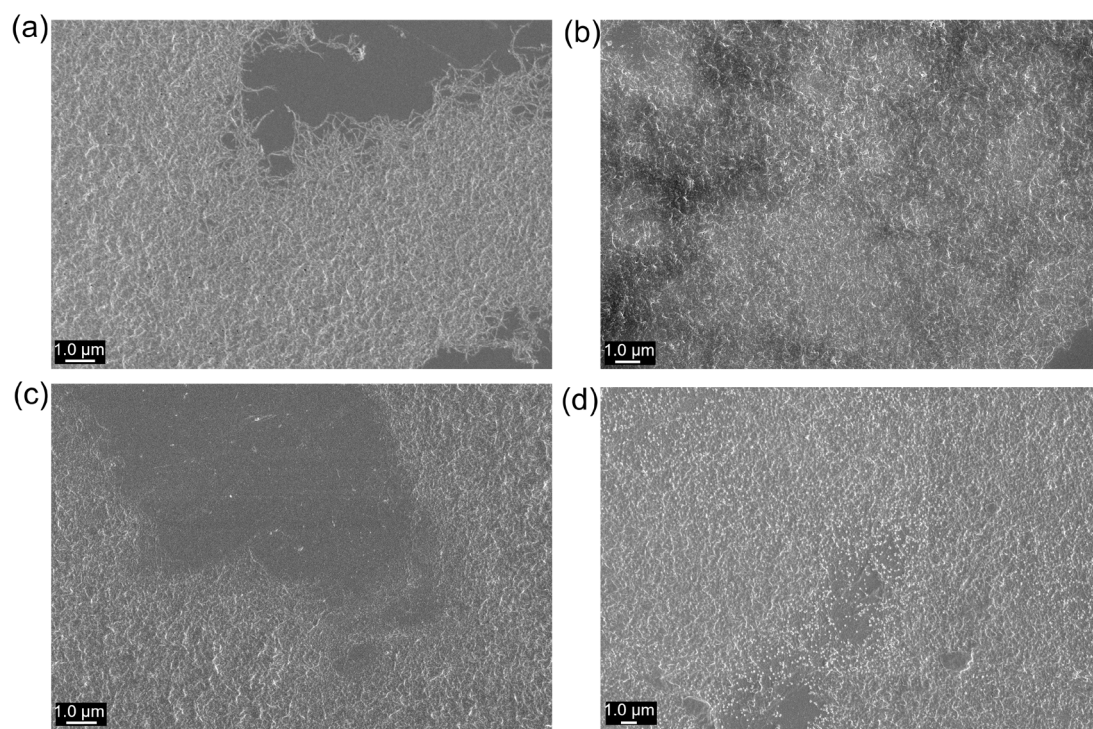


Figure S27. SEM images by changing the e.r. values of *M-1* and *M-2* (*M-1/M-2*) simultaneously, 100%/100% (i.e. **homo**) (a), 80%/80% (b), 60%/60% (c), 50%/50% (i.e. **racemate**) (d). The concentration of each monomer is 0.2 mM.

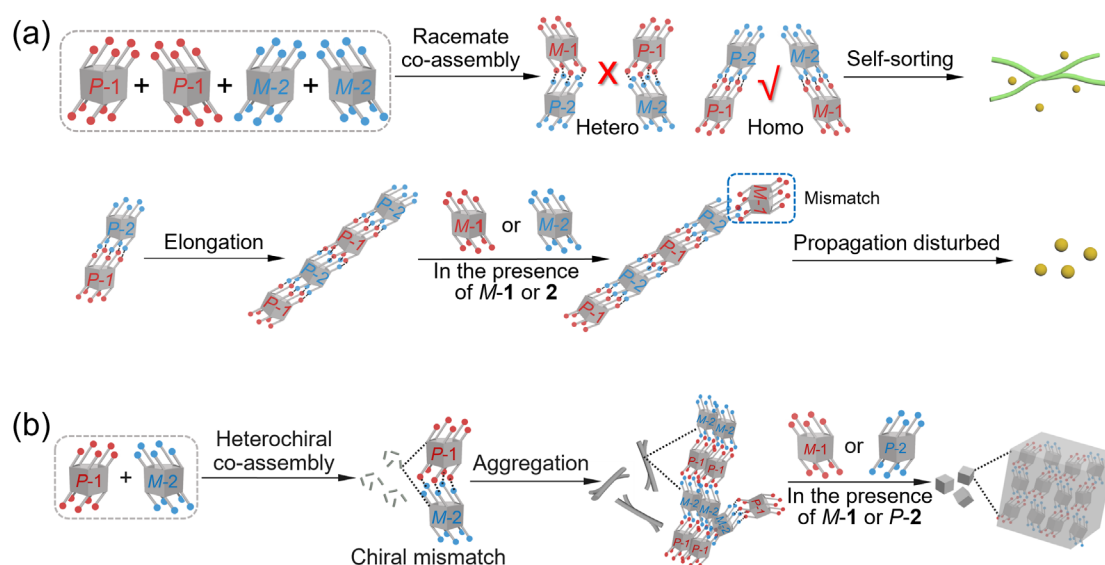


Figure S28. Possible co-assembly pathway for **racemate** (a) and **hetero** combination (b) based on observed morphologies. For **racemate** combination, it shows similar ^1H NMR spectra (Figure S19) and UV-Vis spectra (Figure S7) with **homo** combination, which are significantly different from the **hetero** combination. This result suggests that the helical-sense-matched homochiral binding is favored in the **racemate** combination and resulting in formation of self-sorted nanowires and nanoparticles. However, the inevitable **hetero** binding at the two ends of the kinetically stable **homo** nanowires or oligomers could interrupt the elongation process, resulting in excess thermodynamically stable nanoparticle formation and turn out to be solution. For **hetero** combination, the helical-sense mismatching of P5As results in a nondirectional array of P5A at both ends of the short nanowire, making the propagated longer nanowire unstable, and the irregular morphology provides external binding sites to form branched structures. However, the short-branched nanowire morphology only stable in absolute **hetero** combination. When decrease the e.r. value of **1** in **homo** combination (Figure 4b), the increased **hetero** content as the decrement of e.r. value should increase the content of short nanowire, but the morphology presented to be cubic nanoparticle. We assume that introducing enantiomer of the chiral monomers in the system (i.e., changing the e.r. value of **1** or **2**), the competitive helical-sense-matched binding of the **homo** combination interrupts the formation of short branched nanowire to form more stable nanoparticles (Figure S26).

11. Host-guest effect on homo mixture transformation

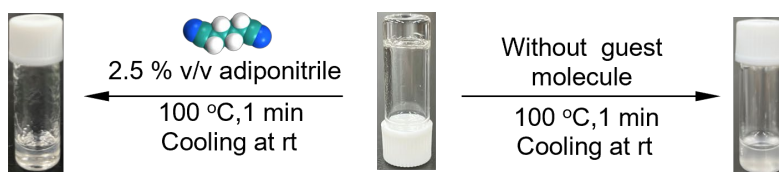


Figure S29. Photographs of **homo** gel transformation under 100 °C for 1 min and then cool down at room temperature. The gel sample with guest molecule remained transparent with partial gel character, while the gel sample without guest molecule totally transformed into turbid solvent.

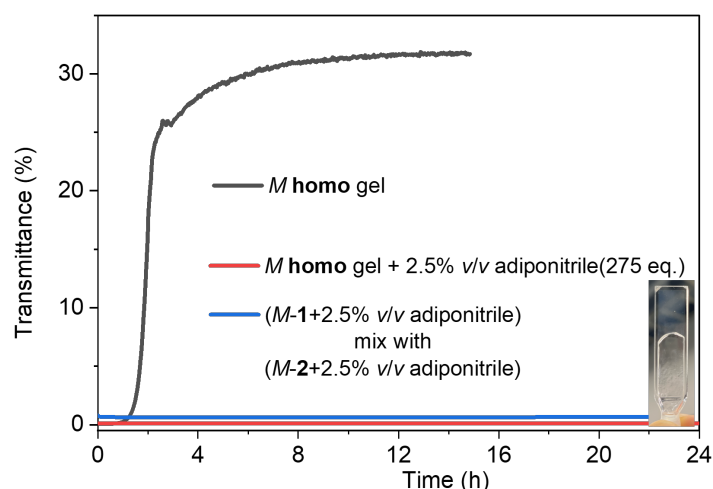


Figure S30. Time dependence of light transmittance for the *M* homo gel (chloroform/DMSO = 1:1 (v/v), each monomer: 0.4 mM) at 60 °C with adiponitrile (black line) and without adiponitrile (red line). The stability of gel prepared by mixing the adiponitrile-*M*-1 complex with adiponitrile-*M*-2 complex is presented in blue line. Inserted image show the physical properties of the gel.

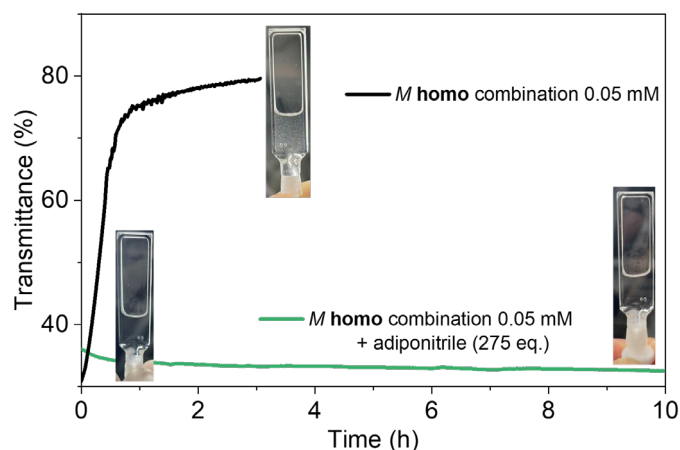


Figure S31. Time dependence of light transmittance for the *M* homo combination in sol state (chloroform/DMSO = 1:1 (v/v), each monomer: 0.05 mM) at 60 °C with adiponitrile (green line) and without adiponitrile (black line). Inserted images show the physical properties of the gels.

12. References

- (S1) Fa, S.; Sakata, Y.; Akine, S.; Ogoshi, T. Non-Covalent Interactions Enable the Length-Controlled Generation of Discrete Tubes Capable of Guest Exchange. *Angew. Chem. Int. Ed.* **2020**, *59*, 9309–9313.
- (S2) Andrei, I.-M.; Strilets, D.; Fa, S.; Baaden, M.; Ogoshi, T.; Barboiu, M. Combinatorial Screening of Water/proton Permeation of Self-assembled Pillar[5]arene Artificial Water Channel Libraries. *Angew. Chem. Int. Ed.* **2023**, *62*, e202310812.
- (S3) Kaizerman-Kane, D.; Hadar, M.; Granot, E.; Patolsky, F.; Zafrani, Y.; Cohen, Y. Shape Induced Sorting via Rim-to-Rim Complementarity in the Formation of Pillar[5, 6]arene-based Supramolecular Organogels. *Org. Chem. Front.* **2019**, *6*, 3348–3354.
- (S4) Fa, S.; Shi, T.-H.; Akama, S.; Adachi, K.; Wada, K.; Tanaka, S.; Oyama, N.; Kato, K.; Ohtani, S.; Nagata, Y.; Akine, S.; Ogoshi, T. Real-time Chirality Transfer Monitoring from Statistically Random to Discrete Homochiral Nanotubes. *Nat. Commun.* **2022**, *13*, 7378.
- (S5) Nagata, Y.; Suzuki, M.; Shimada, Y.; Sengoku, H.; Nishida, S.; Kakuta, T.; Yamagishi, T.; Suginome, M.; Ogoshi, T. Holding of Planar Chirality of Pillar[5]arene by Kinetic Trapping Using Host–guest Interactions with Achiral Guest Solvents. *Chem. Commun.* **2020**, *56*, 8424–8427.