

Supramolecular Polymerization Driven by the Dimerization of Single-stranded Helix to Double-stranded Helix

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Electronic Supplementary Information

Abstract We reported a type of strong and highly directional non-covalent interactions based on the dimerization of single-stranded helix to double-stranded helix that can achieve supramolecular polymerization, giving rise to the formation of linear supramolecular polymers.

Keywords Helix; Double-stranded helix; Supramolecular polymers; Supramolecular polymerization; Dimerization

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Supramolecular polymers consist of repeating monomers bound through non-covalent interactions, such as host-guest^[1–7], multiple hydrogen bonding^[8–13], π - π ^[5, 6, 14–17] interactions, and metal coordination^[18–26], leading to the generation of novel functional supramolecular materials with special features such as reversibility and stimulus-responsibility^[27–33]. However, the synthesis of supramolecular polymers is the bottleneck constraint for the development of functional supramolecular materials. It is a long-standing goal to create powerful non-covalent forces for supramolecular polymerization that enable chemists to develop diverse supramolecular polymer materials. One important contribution on supramolecular polymers toward new materials is to use quadruple hydrogen-bonding units of ureidopyrimidinone with high association constant reported by Meijer and coworkers^[9, 34]. This strong non-covalent force has been widely recognized and applied in the design and creation of functional supramolecular materials^[24, 35–39]. Additionally, Zhang *et al.* developed a series of supramolecular polymers based on host-enhanced charge transfer interactions as well as host-enhanced π - π interactions^[5, 6, 32]. At the same time, by employing host-guest interactions, Huang and coworkers created a number of supramolecular polymer materials with interesting functions^[1, 2, 30]. Furthermore, supramolecular polymers designed by metal coordination can show useful properties which are applicable in optoelectronics and molecular wires^[21, 22].

In despite of some successful supramolecular polymerization methods reported previously^[5, 6, 9, 32, 34, 40–42], the exploration of novel supramolecular polymerization approaches remains challenging. To have very strong and highly directional non-covalent interactions is a prerequisite for synthesizing linear supramolecular polymers rather than gelation and uncontrollable multidirectional association networks. Like the formation of double-stranded DNA, synthetic single-stranded helices are possible to self-organize into double-stranded helix by non-covalent interactions^[43–50]. We have recently developed a kind of helical polymers which can interconvert between single-stranded helix and double-stranded helix driven by intermolecular π - π interactions^[47, 51]. The observation on the formation of stable double-stranded helix through the dimerization of single-stranded helix inspired us to develop strong and highly directional non-covalent interactions for preparing linear supramolecular polymers. Herein, we present a new method for supramolecular polymerization driven by the dimerization of single-stranded helix to double-stranded helix (Fig. 1).

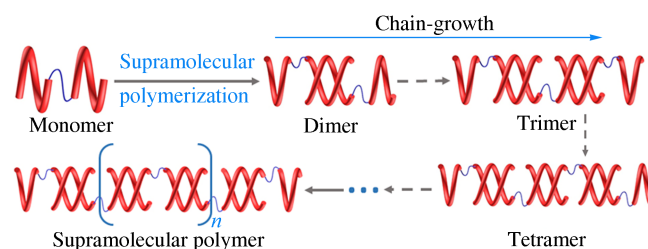


Fig. 1 Schematic representation of a new way of supramolecular polymerization driven by the dimerization of single-stranded helix to double-stranded helix

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A helical heptamer (**1**) (Fig. 2a), which has an identical backbone structure with helical polymers reported previously^[47] (Fig. S1, in electronic supplementary information, ESI), was synthesized according to the multi-step synthesis procedure (Scheme S1, in ESI) and fully characterized. Circular dichroism (CD) measurement was carried out to prove the helical conformation of heptamer (**1**) in solution. As observed, the racemic helical heptamer (**1**) did not have any CD signal (Fig. 2b). When a chiral group (*R*)-1-phenylethanamine was covalently incorporated with the terminal of heptamer (Scheme S2, in ESI), CD spectra gave a negative signal at 370 nm (Fig. 2b), which supported the formation of an induced left-handed helix (**2**). This observation is consistent with previous result in helical polymers^[47]. Since this kind of helical structures is prone to form the double helix by the dimerization of single helix^[47], concentration-dependent fluorescence titration was thus carried out to identify the formation of double helix. As the concentration of heptamer (**1**) increases, the fluorescence intensity of emission wavelength at 475 nm gradually increases, and then turns to decrease with the further increase of the concentration (Fig. S2, in ESI). This result indicated the interconversion from single helix (**1**) to double helix (**1**)₂. Notably, a turn point was found at the concentration of below 10.0 $\mu\text{mol}\cdot\text{L}^{-1}$, suggesting that the dimerization of single helix just happened and the dimerization constant is $10^5\text{ L}\cdot\text{mol}^{-1}$ around. Moreover, a ¹H diffusion-ordered spectroscopy (DOSY) measurement (Fig. S3, in ESI) was employed to check the formation of

double-stranded helix. In both relatively diluted and concentrated chloroform solutions of heptamer (**1**) at 293 K, two diffusion coefficients were found to be 7.51×10^{-10} and $3.43 \times 10^{-10}\text{ m}^2\cdot\text{s}^{-1}$, corresponding to the single helix and the double helix, respectively. In light of the Stokes-Einstein equation, the solvodynamic radius has an approximate 2.19-fold difference (Fig. S4, in ESI), strongly indicating the generation of double helix from single helix^[52].

It is difficult to accurately measure the dimerization constant of single helix (**1**) to double helix (**1**)₂ by common spectroscopic analysis due to the absence of specific signal groups in their structures. We therefore for the first time evaluated the dimerization constant by using the fluorescence lifetime spectroscopy. As shown in Fig. 2(c), two fluorescence lifetimes in the single helix (**1**) system determined from curve fitting of the exponential decay curves were found to be 3.02 and 31.7 ns, corresponding to the single helix (**1**) and double helix (**1**)₂, respectively. At 10.0 $\mu\text{mol}\cdot\text{L}^{-1}$ of (**1**), the molar ratio between single helix (**1**) and double helix (**1**)₂ can be calculated as 59.6%:40.4%. When the concentration of (**1**) increases to 1.0 $\text{mmol}\cdot\text{L}^{-1}$, their molar ratio was changed as 13.2%:86.8% (Fig. S5, in ESI), indicating that the content of double helix (**1**)₂ increased as the concentration of single helix (**1**) was raised. On the basis of above experimental data (Table S1), the dimerization constant of single helix (**1**) self-assembling into double helix (**1**)₂ was calculated to be about $1.2 \times 10^5\text{ L}\cdot\text{mol}^{-1}$ in chloroform. This result is well identified with that obtained from above concentration-dependent fluorescence titration.

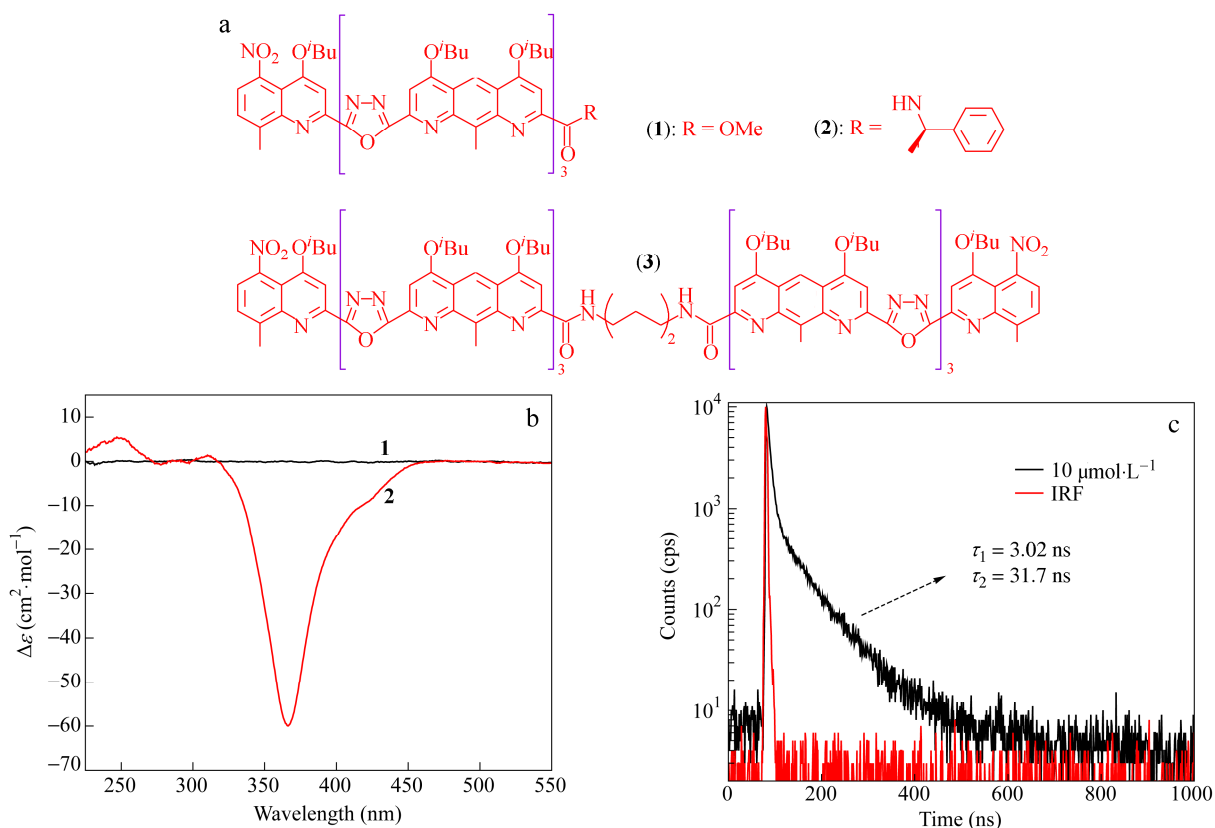


Fig. 2 (a) Molecular structures of helices (**1**)–(**3**) used in this study; (b) CD spectra of helices (**1**) and (**2**); (c) Fluorescence life-time spectroscopy of heptamer (**1**) (10.0 $\mu\text{mol}\cdot\text{L}^{-1}$) in chloroform with an excitation wavelength of 375 nm

Actually, the dimerization constant can be largely enhanced by increasing the helix length or changing solvent polarity^[43, 49], which is able to thus provide strong enough driving forces for supramolecular polymerization.

In order to demonstrate the new supramolecular polymerization method (Fig. 1), a dumbbell-shape supramolecular monomer, consisting of two helical segments as the associating end groups and an aliphatic linker, was preliminarily designed and synthesized (Scheme S3, in ESI). The aliphatic linker hexane-1,6-diamine was selected to covalently connect two heptamer molecules, resulting in the generation of supramolecular monomer (**3**) (Fig. 2a and Fig. S6, in ESI). The supramolecular polymerization of (**3**) was thus monitored by nuclear magnetic resonance (NMR) spectroscopy. As observed in the ¹H-NMR spectra (Fig. S7, in ESI), the broadened and weakened peaks compared to the monomer (**3**) indicate the formation of supramolecular aggregates. The phenomenon is the same with traditional polymerization. When a little amount of trifluoroacetic acid was added to break the aggregation, the NMR signals are clearly consistent with the structure of supramolecular monomer (**3**). Therefore, NMR study demonstrated that the self-assembly of supramolecular monomer (**3**) did take place. In order to reveal the supramolecular polymerization process, matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) analysis was carried out. Surprisingly, MALDI-TOF MS results provided direct evidences on the supramolecular polymerization of monomer (**3**) in solution. The supramolecular polymers, like dimer, trimer, and tetramer, formed by supramolecular polymerization of monomer (**3**), can be definitely detected, respectively (Fig. S8, in ESI). In particular, both trimer and tetramer are typical supramolecular oligomers with molecular weights of about 10 kD. This result demonstrated a chain-growth supramolecular polymerization, which will form linear supramolecular polymers. Very strikingly, a linear supramolecular polymer can be directly visualized by atomic force microscopy (AFM) measurement (Fig. 3). The height of supramolecular polymer contour in the AFM image was measured to be 2.44 nm (Fig. 3 and Fig. S9 in ESI), well

matching with the diameter of helix as reported previously in the helical polymer system^[47]. This observation revealed a chain-growth supramolecular polymerization of monomer (**3**), giving rise to the formation of a single linear supramolecular polymer. At the same time, the linear supramolecular polymers enable further self-assemble into fibers, as observed by both transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (Figs. 3c–3e). Furthermore, dynamic light scattering (DLS) experiments (Fig. S10 in ESI) supported the formation of supramolecular polymers, as evidenced by that the hydrated radius increased up to 300 nm as the concentration of monomer (**3**) increases. These observations demonstrated that the supramolecular polymerization can be driven by the dimerization of single-stranded helix to double-stranded helix through spiral π - π interactions.

In conclusion, we developed a type of strong and highly directional non-covalent interactions based on the dimerization of single-stranded helix to double-stranded helix. The dimerization constant of a short helical strand self-assembling into double-helical homodimer was measured to be as high as $10^5 \text{ L} \cdot \text{mol}^{-1}$ in this study, and could be largely enhanced, which thus provided strong and highly directional driving forces for supramolecular polymerization. MALDI-TOF MS analysis of a dumbbell-shape supramolecular monomer clearly revealed a chain-growth supramolecular polymerization process in the case, and particularly the tetramer, as a typical supramolecular polymer has the molecular weight of up to 13 kD. AFM measurement showed a linear supramolecular polymer that can further self-assemble into the fibers. This study has developed a novel and versatile supramolecular polymerization method for synthesizing linear supramolecular polymers through the dimerization of single-stranded helix to double-stranded helix. On the basis of such strong and highly directional non-covalent interactions reported above, governing the spatial architectures of helix-based supramolecular monomers to prepare supramolecular polymers with controllable topologies is under investigation.

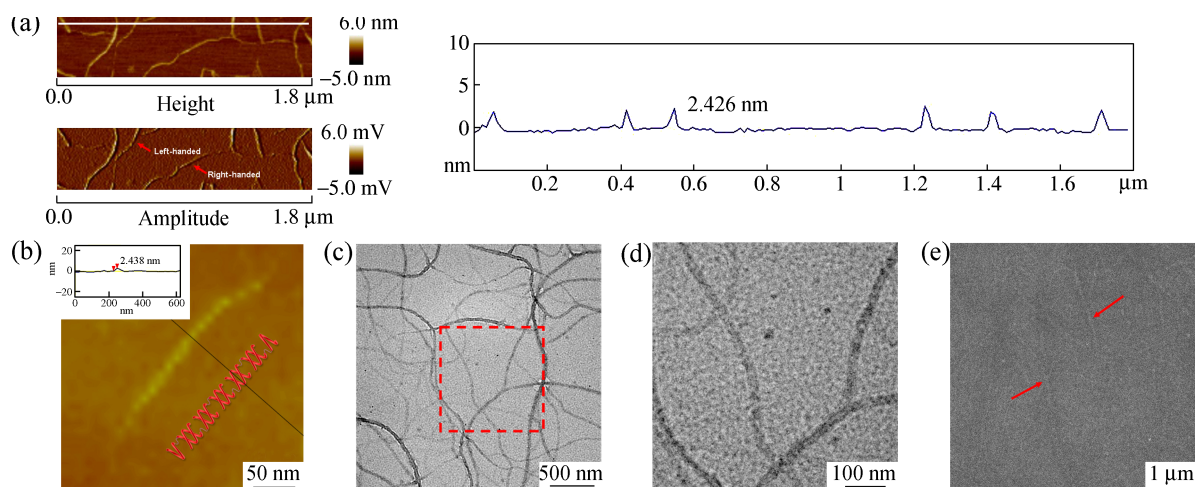


Fig. 3 Imaging of supramolecular polymers formed by supramolecular polymerization of monomer (**3**): (a) AFM images of linear supramolecular polymers with helicity and the height profile; (b) Magnifying AFM image of a supramolecular polymer; (c, d) TEM images of supramolecular polymers; (e) SEM image of supramolecular polymers

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at: <https://doi.org/10.1007/s10118-018-2058-2>.

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REFERENCES

- Yan, X.; Cook, T. R.; Pollock, J. B.; Wei, P.; Zhang, Y.; Yu, Y.; Huang, F.; Stang, P. J. Responsive supramolecular polymer metallogel constructed by orthogonal coordination-driven self-assembly and host/guest interactions. *J. Am. Chem. Soc.* 2014, 136, 4460–4463.
- Zhang, M.; Xu, D.; Yan, X.; Chen, J.; Dong, S.; Zheng, B.; Huang, F. Self-healing supramolecular gels formed by crown ether based host-guest interactions. *Angew. Chem.* 2012, 124, 7117–7121.
- Nakahata, M.; Takashima, Y.; Yamaguchi, H.; Harada, A. Redox-responsive self-healing materials formed from host-guest polymers. *Nat. Commun.* 2011, 2, 511–517.
- Sun, R.; Xue, C.; Ma, X.; Gao, M.; Tian, H.; Li, Q. Light-driven linear helical supramolecular polymer formed by molecular-recognition-directed self-assembly of bis(*p*-sulfonatocalix[4]arene) and pseudorotaxane. *J. Am. Chem. Soc.* 2013, 135, 5990–5993.
- Liu, Y.; Yu, Y.; Gao, J.; Wang, Z.; Zhang, X. Water-soluble supramolecular polymerization driven by multiple host-stabilized charge-transfer interactions. *Angew. Chem. Int. Ed.* 2010, 49, 6576–6579.
- Huang, Z.; Yang, L.; Liu, Y.; Wang, Z.; Scherman, O. A.; Zhang, X. Water-soluble supramolecular polymerization driven by multiple host-stabilized charge-transfer interactions. *Angew. Chem. Int. Ed.* 2014, 53, 5351–5355.
- Chen, L.; Huang, Z.; Xu, J.; Wang, Z.; Zhang, X. Controllable supramolecular polymerization through self-sorting of aliphatic and aromatic motifs. *Polym. Chem.* 2016, 7, 1397–1404.
- Fouquey, C.; Lehn, J. M.; Levelut, A. M. Molecular recognition directed self-assembly of supramolecular liquid crystalline polymers from complementary chiral components. *Adv. Mater.* 1990, 2, 254–257.
- Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. Reversible polymers formed from self-complementary monomers using quadruple hydrogen bonding. *Science* 1997, 278, 1601–1604.
- Corbin, P. S.; Zimmerman, S. C. Self-Association without regard to prototropy. A heterocycle that forms extremely stable quadruply hydrogen-bonded dimers. *J. Am. Chem. Soc.* 1998, 120, 9710–9711.
- Berl, V.; Schmutz, M.; Krische, M. J.; Khoury, R. G.; Lehn, J. M. Supramolecular polymers generated from heterocomplementary monomers linked through multiple hydrogen-bonding arrays-formation, characterization, and properties. *Chem. Eur. J.* 2002, 8, 1227–1244.
- Sherrington, D. C.; Taskinen, K. A. Self-assembly in synthetic macromolecular systems via multiple hydrogen bonding interactions. *Chem. Soc. Rev.* 2001, 30, 83–93.
- Schmuck, C.; Wienand, W. Self-complementary quadruple hydrogen-bonding motifs as a functional principle: from dimeric supramolecules to supramolecular polymers. *Angew. Chem. Int. Ed.* 2001, 40, 4363–4369.
- Burattini, S.; Greenland, B. W.; Merino, D. H.; Weng, W.; Seppala, J.; Colquhoun, H. M.; Hayes, W.; Mackay, M. E.; Hamley, I. W.; Rowan, S. J. A healable supramolecular polymer blend based on aromatic π - π stacking and hydrogen-bonding interactions. *J. Am. Chem. Soc.* 2010, 132, 12051–12058.
- Burattini, S.; Colquhoun, H. M.; Fox, J. D.; Friedmann, D.; Greenland, B. W.; Harris, P. J. F.; Hayes, W.; Mackay, M. E.; Rowan, S. J. A self-repairing supramolecular polymer system: healability as a consequence of donor-acceptor π - π stacking interactions. *Chem. Commun.* 2009, 6717–6719.
- Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. About supramolecular assemblies of π -conjugated systems. *Chem. Rev.* 2005, 105, 1491–1546.
- Burattini, S.; Greenland, B. W.; Hayes, W.; Mackay, M. E.; Rowan, S. J.; Colquhoun, H. M. A supramolecular polymer based on Tweezer-type π - π stacking interactions: molecular design for healability and enhanced toughness. *Chem. Mater.* 2011, 23, 6–8.
- Chen, X. M.; Liu, G. F. Double-stranded helices and molecular zippers assembled from single-stranded coordination polymers directed by supramolecular interactions. *Chem. Eur. J.* 2002, 8, 4811–4817.
- Wang, F.; Zhang, J.; Dong, S.; Shu, J.; Liu, M.; Gibson, H. W.; Huang, F. Metal coordination mediated reversible conversion between linear and cross-linked supramolecular polymers. *Angew. Chem. Int. Ed.* 2010, 49, 1090–1094.
- Liu, Y.; Huang, Z.; Tan, X.; Wang, Z.; Zhang, X. Cucurbit[8]uril-based supramolecular polymers: promoting supramolecular polymerization by metal-coordination. *Chem. Commun.* 2013, 49, 5766–5768.
- de Hatten, X.; Asil, D.; Friend, R. H.; Nitschke, J. R. Aqueous self-assembly of an electroluminescent double-helical metallopolymer. *J. Am. Chem. Soc.* 2012, 134, 19170–19178.
- Kaminker, R.; de Hatten, X.; Lahav, M.; Lupo, F.; Gulino, A.; Evmenenko, G.; Dutta, P.; Browne, C.; Nitschke, J. R.; van der Boom, M. E. Assembly of surface-confined homochiral helicates: chiral discrimination of DOPA and unidirectional charge transfer. *J. Am. Chem. Soc.* 2013, 135, 17052–17059.
- Zhou, Z.; Yan, X.; Cook, T. R.; Saha, M. L.; Stang, P. J. Engineering functionalization in a supramolecular polymer: hierarchical self-organization of triply orthogonal non-covalent interactions on a supramolecular coordination complex platform. *J. Am. Chem. Soc.* 2016, 138, 806–809.
- Yan, X.; Li, S.; Pollock, J. B.; Cook, T. R.; Chen, J.; Zhang, Y.; Ji, X.; Yu, Y.; Huang, F.; Stang, P. J. Supramolecular polymers with tunable topologies via hierarchical coordination-driven self-assembly and hydrogen bonding interfaces. *Proc. Natl. Acad. Sci. U. S. A.* 2013, 110, 15585–15590.
- Li, S. L.; Xiao, T.; Lin, C.; Wang, L. Advanced supramolecular polymers constructed by orthogonal self-assembly. *Chem. Soc. Rev.* 2012, 41, 5950–5968.
- Zhang, J.; Su, C. Metal-organic gels: from discrete metallogelators to coordination polymers. *Coord. Chem. Rev.* 2013, 257, 1373–1408.
- de Greef, T. F. A.; Smulders, M. M. J.; Wolffs, M.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W. supramolecular polymerization. *Chem. Rev.* 2009, 109, 5687–5754.
- Whittell, G. R.; Hager, M. D.; Schubert, U. S.; Manners, I. Functional soft materials from metallopolymer and metallosupramolecular polymers. *Nat. Mater.* 2011, 10, 176–188.
- Aida, T.; Meijer, E. W.; Stupp, S. I. Functional supramolecular

- polymers. *Science* 2012, 335, 813–817.
- 30 Yan, X.; Wang, F.; Zheng, B.; Huang, F. Stimuli-responsive supramolecular polymeric materials. *Chem. Soc. Rev.* 2012, 41, 6042–6065.
 - 31 Appel, E. A.; del Barrio, J.; Loh, X. J.; Scherman, O. A. Supramolecular polymeric hydrogels. *Chem. Soc. Rev.* 2012, 41, 6195–6214.
 - 32 Yang, L.; Tan, X.; Wang, Z.; Zhang, X. Supramolecular polymers: historical development, preparation, characterization, and functions. *Chem. Rev.* 2015, 115, 7196–7239.
 - 33 Lehn, J. M. Perspectives in chemistry—aspects of adaptive chemistry and materials. *Angew. Chem. Int. Ed.* 2015, 54, 3276–3289.
 - 34 Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W. Strong dimerization of ureidopyrimidones *via* quadruple hydrogen bonding. *J. Am. Chem. Soc.* 1998, 120, 6761–6769.
 - 35 Xu, J. F.; Chen, Y. Z.; Wu, D. Y.; Wu, L. Z.; Tung, C. H.; Yang, Q. Z. Photoresponsive hydrogen-bonded supramolecular polymers based on a stiff stilbene unit. *Angew. Chem. Int. Ed.* 2013, 52, 9738–9742.
 - 36 Sánchez, L.; Martín, N.; Guldi, D. M. Hydrogen-bonding motifs in fullerene chemistry. *Angew. Chem. Int. Ed.* 2005, 44, 5374–5382.
 - 37 Rispens, M. T.; Sánchez, L.; Knol, J.; Hummelen, J. C. Supramolecular organization of fullerenes by quadruple hydrogen bonding. *Chem. Commun.* 2001, 2, 161–162.
 - 38 González, J. J.; González, S.; Priego, E. M.; Luo, C.; Guldi, D. M.; de Mendoza, J.; Martín, N. A new approach to supramolecular C60-dimers based in quadruple hydrogen bonding. *Chem. Commun.* 2001, 2, 163–164.
 - 39 Yan, X.; Jiang, B.; Cook, T.R.; Zhang, Y.; Li, J.; Yu, Y.; Huang, F.; Yang, H. B.; Stang, P. J. Dendronized organoplatinum(II) metallacyclic polymers constructed by hierarchical coordination-driven self-assembly and hydrogen-bonding interfaces. *J. Am. Chem. Soc.* 2013, 135, 16813–16816.
 - 40 Zhang, Z.; Luo, Y.; Chen, J.; Dong, S.; Yu, Y.; Ma, Z.; Huang, F. Formation of linear supramolecular polymers that is driven by C[BOND]H π interactions in solution and in the solid state. *Angew. Chem.* 2011, 123, 1433–1437.
 - 41 Lehn, J. M. Perspectives in chemistry—aspects of adaptive chemistry and materials. *Angew. Chem. Int. Ed.* 2015, 54, 3276–3289.
 - 42 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.
 - 43 Singleton, M. L.; Pirotte, G.; Kauffmann, B.; Ferrand, Y.; Huc, I. Increasing the Size of an Aromatic Helical Foldamer Cavity by Strand Intercalation. *Angew. Chem. Int. Ed.* 2014, 53, 13140–13144.
 - 44 Berl, V.; Huc, I.; Khoury, R.; Krische, M. J.; Lehn, J. M. Interconversion of single and double helices formed from synthetic molecular strands. *Nature* 2000, 407, 720–723.
 - 45 Yamada, H.; Wu, Z. Q.; Furusho, Y.; Yashima, E. Thermodynamic and kinetic stabilities of complementary double helices utilizing amidinium-carboxylate salt bridges. *J. Am. Chem. Soc.* 2012, 134, 9506–9520.
 - 46 Yashima, E.; Maeda, K.; Furusho, Y. Single- and double-stranded helical polymers: synthesis, structures, and functions. *Acc. Chem. Res.* 2008, 41, 1166–1180.
 - 47 Zhu, J. Y.; Dong, Z. Y.; Lei, S. B.; Cao, L. L.; Yang, B.; Li, W. F.; Zhang, Y. C.; Liu, J. Q.; Shen, J. C. Design of aromatic helical polymers for STM visualization: imaging of single and double helices with a pattern of p-p stacking. *Angew. Chem. Int. Ed.* 2015, 54, 3097–3101.
 - 48 Baptiste, B.; Zhu, J.; Haldar, D.; Kauffmann, B.; Léger, J. M.; Huc, I. Hybridization of long pyridine-dicarboxamide oligomers into multi-turn double helices: slow strand association and dissociation, solvent dependence, and solid state structures. *Chem. Asian J.* 2010, 5, 1364–1375.
 - 49 Shang, J.; Gan, Q.; Dawson, S. J.; Rosu, F.; Jiang, H.; Ferrand, Y.; Huc, I. Self-association of aromatic oligoamide foldamers into double helices in water. *Org. Lett.* 2014, 16, 4992–4995.
 - 50 Yashima, E.; Ousaka, N.; Taura, D.; Shimomura, K.; Ikai, T.; Maeda, K. Supramolecular helical systems: helical assemblies of small molecules, foldamers, and polymers with chiral amplification and their functions. *Chem. Rev.* 2016, 116, 13752–13990.
 - 51 Lang, C.; Li, W. F.; Dong, Z. Y.; Zhang, X.; Yang, F. H.; Yang, B.; Deng, X. L.; Zhang, C. Y.; Xu, J. Y.; Liu, J. Q. Biomimetic transmembrane channels with high stability and transporting efficiency from helically folded macromolecules. *Angew. Chem. Int. Ed.* 2016, 55, 9723–9727.
 - 52 The length of double helix will be 2-fold longer compared to the single helix, as evidenced by X-ray structure studies, related to see Ref. 43, 44, and 48.