Self-Assembly of Supramolecular Polymers into Tunable Helical Structures

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ABSTRACT: There is growing interest in the design of synthetic molecules that are able to self-assemble into a polymeric chain with compact helical conformations, which is analogous to the folded state of natural proteins. Herein, we highlight supramolecular approach to the formation of helical architectures and their conformational changes driven by external stimuli. Helical organization in synthetic self-assembling systems can be achieved by the various types of noncovalent interactions, which include hydrogen bonding, solvophobic effects, and metal-ligand interactions. Since the external environment can have a large influence on the strength and configuration of noncovalent interactions between the individual components, stimulus-induced alterations in the intramolecular noncovalent interactions can result in dynamic conformational change of the supramolecular helical structure thus, driving significant changes in the properties of the materials. Therefore, these supramolecular helices hold great promise as stimuli-responsive materials. © 2008 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 46: 1925–1935, 2008

Keywords: coordination polymer; helical conformation; oligomers; self-assembly; supramolecular structures

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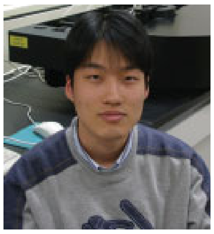

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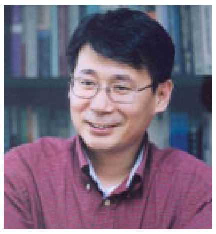

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INTRODUCTION

Creation of supramolecular architectures with well-defined shape and size has been one of the major research focuses in areas related to materials science, nanochemistry, and biomimetic or bioinspired chemistry.[1–9] In particular, one of the most significant recent highlights in the field of supramolecular chemistry is the development of folded helical structures, which are important modules for the construction of functional nano-objects such as nanotubes, nanowires, and nanomachines.[10–15] Helical architectures ideally suited for the design of the responsive materials since the dynamic and reversible conformational changes can be triggered by external environmental conditions. It has been observed that the induced conformational transition often resulted in changes in the optical and mechanical properties of the material.[16,17]

The helical architectures can be constructed by several approaches.[18,19] The simplest example is a foldamer from synthetic polymers and oligomers of flexible conformational skeletons.[20–27] These molecules are folded into helical conformations by a variety of intramolecular noncovalent interactions including electrostatic, solvophobic effect, and hydrogen bonds. The dynamic nature of these supramolecular helical materials allows external conditions to influence their behavior in a way that is not achievable with traditional covalent macromolecules. Another strategy of inducing helical conformation is a supramolecular polymerization process, which occurs between monomeric building blocks through a strong directional interaction, such as hydrogen bonding, dye–dye interactions, and metal–ligand coordination.[28–31] For example, elongated supramolecular polymers formed by the directional interaction between monomers, adopt a helical folding through an additional stabilizing interaction such as π–π interaction, and display behaviors that only macromolecules have such as the occurrence of gelation and the increases in mechanical strength. Metal-ligand coordination can also provide an excellent means of forming supramolecular helical architecture as the coordination bond is relatively strong and directional.[32–37] Furthermore, as the ligand structures can be varied in a desired manner, their kinetic stability and material properties can be fine-tuned with the structures of appropriately designed ligands and the types of metal ions.

In this highlight, we will mainly focus on the helical conformations that are achievable by supramolecular secondary interactions. In addition, we will especially discuss about responsive helical conformations, whose conformations and material properties are reversibly transformed by the external stimuli.

FOLDAMERS FROM OLIGOMERS AND POLYMERS

Helical conformations have been observed in many synthetic polymers as well as biopolymers.[38–43] Percec et al. have reported a library of dendronized polyphenylacetylene (PPA)s that exhibit chiral helical conformations both in solution and in solid (Fig. 1).[44,45] The high cis-content stereoregular PPAs were synthesized with dendritic acetylene monomers and they were polymerized using $[Rh(nbd)Cl]_2$. In methyl cyclohexane solution, PPAs adopt preferred helix screw sense which is confirmed by circular dichroism (CD). The helical order has also identified by XRD studies in bulk state, suggesting that the PPAs behaved as cylindrical objects that self-organize into columnar phase. The helical arrangement was enforced by the polyene backbone and the dendritic side groups driven by high cis-content of stereoregular *cis*-transoidal dendronized polyacetylenes.

Research on oligomeric foldamers was pioneered by Moore and Gellman groups.[46–52] An example includes the amphiphilic *meta*-linked oligo (*m*-phenylene ethylene)s (OPEs) that can self-assemble into a helical conformation by combination of solvophobic effect and π–π interactions.[47] The formations of these helical conformations were confirmed by several spectroscopic techniques, including UV–vis absorption, fluorescence, and CD spectroscopies. OPE series were connected with its triethylene glycol side chain through a benzoate linkage, because ethylene oxide chains are known to have good solubility in polar solvents. Thereby, the OPE oligomers can be folded into a helical conformation in polar acetonitrile, whereas disordered random conformations pre-

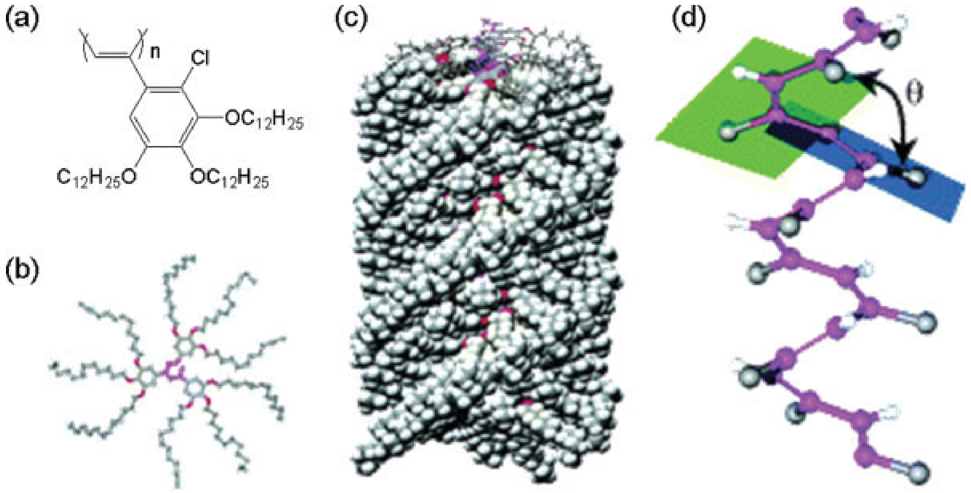

Figure 1. Structure of the PPA; P[(3,4,5)12G1-A]. (a) Chemical structure, (b) top view of a column stratum, (c) side-view renderings as space filling models, and (d) detail of the polymer backbone. Reproduced from ref. 44, with permission from American Chemical Society (2006).

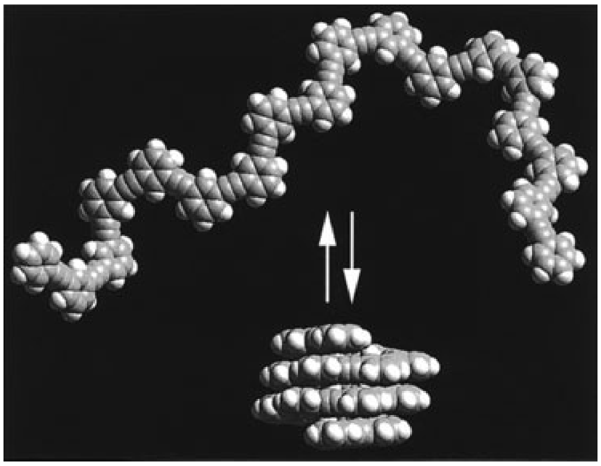

Figure 2. Conformational change of meta-linked oligo (*m*-phenylene ethylene)s. Reproduced from ref. 47, with permission from American Chemical Society (1999).

dominated in chloroform (Fig. 2). In addition, OPE chains exhibited a length-dependent behavior expected from a helical conformation since the intramolecular π-stacking interactions that stabilize the folded structure are not present until the chain length ($\sim$ 10 monomer units) exceeds at least one helical turn.

Another class is represented by the aromatic oligomers reported by Huc and coworkers.[53–56] and Meijer and coworkers,[57–59] where π–π stacking interactions combined with hydrogen-bonding interactions direct folding. Huc and coworkers reported that oligoamide strands composed of alternating 2,6-bis(carbonylamino) pyridine units and 2,6-pyridinedicarboxamide units self-organized into single stranded helical structures upon forming intramolecular hydrogen bonds (Fig. 3).[56] In the pyridine, 2,6-dicarboxamide series, the nitrogen atoms are expected to form hydrogen bond to the neighboring amide hydrogens. These intramolecular hydrogen bonds induce direct rotations about the CO-aryl linkages toward a bent conformation and favor a helical shape of the oligomers. Similar to the oligoamide, Meijer and coworkers reported a helical foldamer based on poly (ureidophthalimide)s in which the urea linker adopts a cisoid conformation due to intramolecular hydrogen bonding (Fig. 4).[58] Molecuar modeling studies and an X-ray structural analysis strongly supported the curved and coplanar conformation of the helical backbone. This curvature lead to a helical arrangement for longer oligomers with lengths exceeding 7–9 units, where it is proposed that π–π interactions further stabilize the helical architecture once a turn is completed.

Another strategy of forming hydrogen bonded foldamer can be found in poly- and oligo(*m*-ethynylpyridine)s cases, in which case the monomeric units fold into a well-ordered helical structure in nonpolar solvent by hydrogen-bonding interactions with guest molecule (Fig. 5).[60] The poly(*m*-ethynylpyridine)s would normally adopt unfolded conformations because every nitrogen atom in pyridine is mainly located at the opposite sides of the ethynediyl bonds to cancel the dipoles. However, when the polymers meet with a saccharide, transition from the disordered state to the ordered helical state was driven by hydrogen-bonding with saccharides, and the chiral sense of the helices was transferred from the bound saccharides. Interestingly, the helices could distinguish glucosides and even native glucose from other monosaccharides and/or their derivatives, illustrating the glucose-specific detection.

SUPRAMOLECULAR POLYMERIZED HELICAL STRUCTURES

One of the simple but powerful concepts in helical polymer is the supramolecular polymerization process between bifunctional monomers of strong binding constant. Consequently, the interactions between these end groups can result in the self-assembly of the monomer units into supramolecular polymers in which noncovalent bonds are an integral part of the polymeric backbone. The properties of such noncovalently bonded polymers have a strong dependence not only on their core components, but also on the nature of the supramolecular interactions. A wide range of noncovalent forces, from simple hydrophobic interactions to more complex

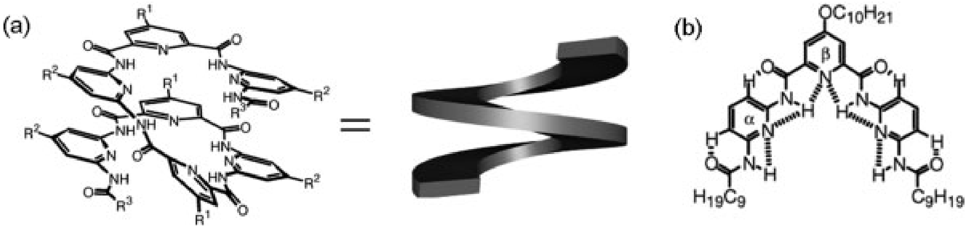

Figure 3. (a) Structure of helical conformation of heptameric oligoamide folded by intramolecular hydrogen bonds and (b) a detailed hydrogen-bonding unit. Reproduced from ref. 56, with permission from Nature Publishing Group (2000).

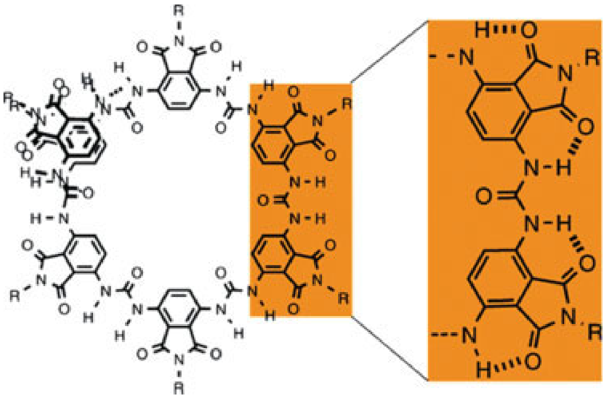

Figure 4. Helical conformation of Poly(ureidophthalimide)s and a detailed hydrogenbonding unit. Reproduced from ref. 58, with permission from Royal Society of Chemistry (2004).

hydrogen bonding interactions, have been utilized to build such supramolecular polymers.

In one approach, Würthner and coworkers reported the formation of self-assembled helical structure as a result of intermolecular dipolar dye–dye interactions (Fig. 6).[28,29] In this supramolecular polymer, each of the two merocyanine units in one monomer dimerize with another dye in an antiparallel fashion, thereby resulting in the formation of polymeric chains that are folded into helical conformations in a nonpolar solvent. Since the solvent polarity influences the strength of noncovalent dipole–dipole interaction, the changes in solvent polarity can induce structural growth from the molecular to the macroscopic scale. In THF, a polar solvent, dyes are dissolved as monomeric compounds, while in methylcyclohexane, a nonpolar solvent, dyes self-assemble into polymeric chains. On the basis of the molecular modeling study and the experimental results from AFM and XRD, six of supramolecular polymeric chains were shown to laterally assemble to give a tubular dye aggregate with a pitch of 5 nm.

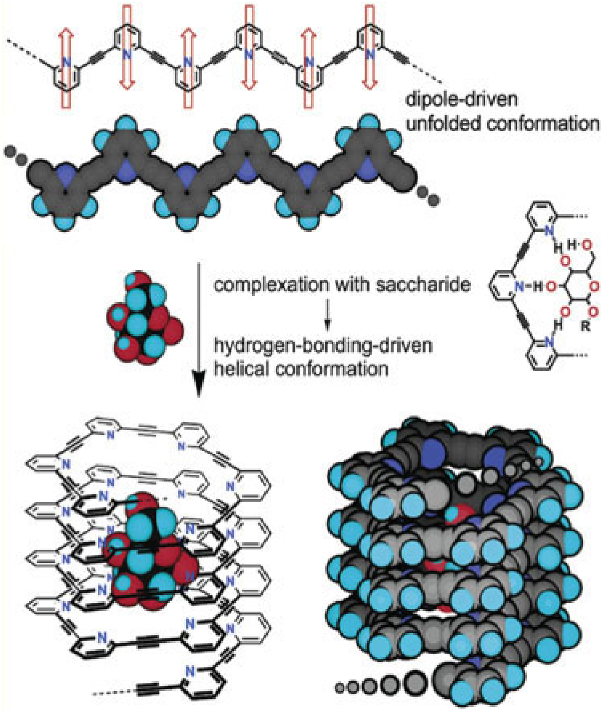

Figure 5. Conformational change of poly(*m*-ethynylpyridine) driven by the complexation with saccharide. Reproduced from ref. 60, with permission from American Chemical Society (2004).

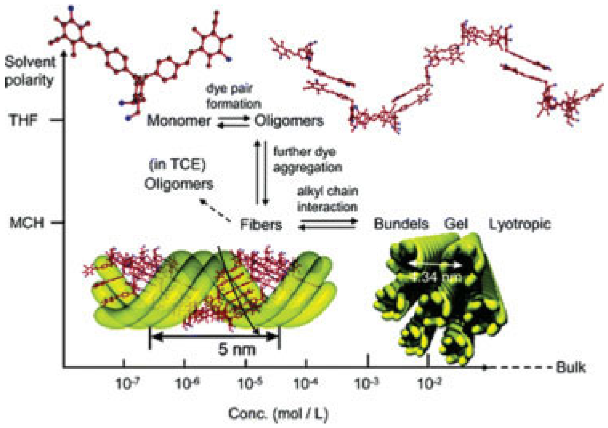

Figure 6. Structural models of different levels of organization observed in bis(merocyanine) dye, which are dependent on the solvent polarity and the concentration. Reproduced from ref. 28, with permission from American Chemical Society (2004).

Meijer and coworkers constructed supramolecularly polymerized helix that is stabilized by quadruple hydrogen bonds between bifunctionalized ureidotriazine units (Fig. 7).[30,31] The relatively strong dimerization capability and the simple preparation of ureidotriazines are attractive features of using of this unit as bifunctional compounds, which can assemble into linear polymeric aggregates. They termed this is as "supramolecular polymers." The monomers consist of bifunctionalized ureidotriazine units connected by a spacer and carry solubilizing chains at the periphery.[61,62] This design allows dimerization through self-complementary quadruple hydrogen bonding among the units and solvophobically induced stacking of the dimers into columnar polymeric architectures, whose structure and helicity can be adjusted by tuning the nature of the solubilizing side chains.

COORDINATION HELICAL STRUCTURES

Coordination interactions, such as complexation between conformationally restricted bent shaped ligands

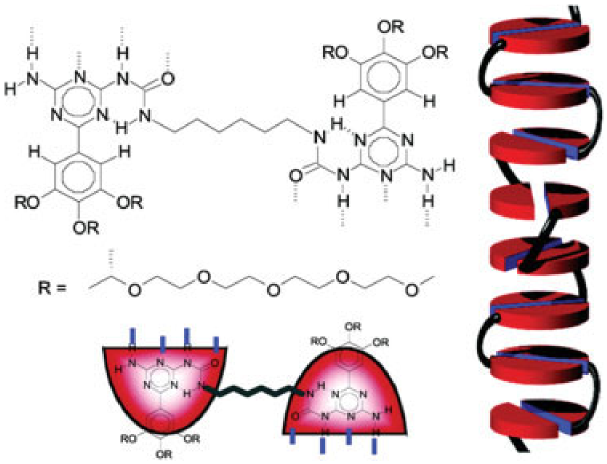

Figure 7. Proposed model of association of bifunctional ureidotriazine molecules in water into helical columns. Reproduced from ref. 61, with permission from Nature Publishing Group (2000).

and transition metals that adopt a linear coordination geometry, can also give rise to extended polymeric chains with a helical structure. Lin and coworkers showed that the twisted binding sites of chiral rigid ditopic bridging ligands based on the 1,1′-binaphthyl unit can be complexed into helical structures by linkage with a linear metal-connecting point.[36] The crystal structure of the complex of 1,1-binaphthyl-6,6′-bipyridines ligand unit and a Ni(II) ion demonstrated the formation of an infinite helical chain in which there are four ligands for each turn of the helix. Mirkin and coworkers reported a homochiral helical polymer complex that can be spontaneously and reversibly transformed into a triangular macrocyclic complex simply through the addition of the appropriate solvent (Fig. 8).[35] The chiral building block ligand was self-assembled into the helical polymer as a 60° corner formed via complexation between its carboxylate groups and $Cu(OAc)_2\bullet 6H_2O$ in a 10:1 mixture of methanol and pyridine, while a 3:10 mixture of solvents yielded triangular macrocycles. The major difference between the connecting metal centers in these two structures is a weakly coordinating axial ligand to the Cu ion that interconnects the carboxylate groups on the periphery of the salen precursors. In the case of helical polymer, the axial ligand is methanol which leads to the formation of the asymmetric unit consisting of a Cu^{2+} ion and a Cu salen moiety, where one carboxylate group coordinates to a second Cu^{2+} ion, while in macrocycles, pyridine was used as an axial ligand driving the formation of symmetric macrocycle. Furthermore, the interconversion between the molecular and polymeric structures is a highly reversible process, which was dependent on the solvent composition.

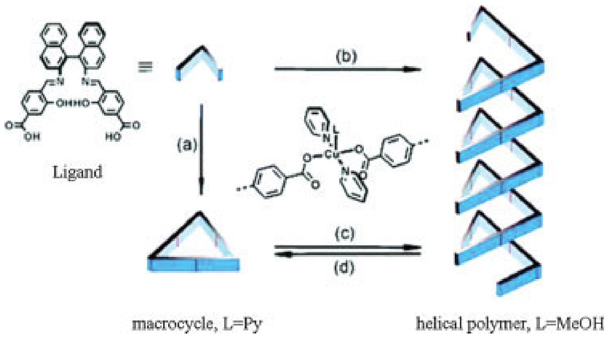

Figure 8. Solvent-mediated reversible interconversion between the triangular macrocycle and the helical polymer. (a) $Cu(OAc)2\bullet 6H_2O$, MeOH/pyridine) 3/10; (b) $Cu(OAc)_2\bullet 6H_2O$, MeOH/pyridine) 10/1; (c) MeOH; (d) pyridine. Reproduced from ref. 35, with permission from American Chemical Society (2007).

We have recently reported that a conformationally flexible, bent-shaped bipyridine ligand containing a dendritic aliphatic side chain has been synthesized as a ligand and complexed with silver ion through a self-assembling process (Fig. 9).[37] The resulting complexes self-assembled into ordered structures that change their shape as a function of the counteranion size in the solid state. The coordination chains based on small anions such as nitrate and tetrafluoroborate self-assemble into helical chains that organize into a 2D hexagonal lattice. The complex based on triflate anion forms dimeric cycles, which stack atop one another to make columns that laterally assemble in a hexagonal fashion. In contrast to the complexes based on small counteranions, the coordination chain based on a larger anion, heptafluoro-

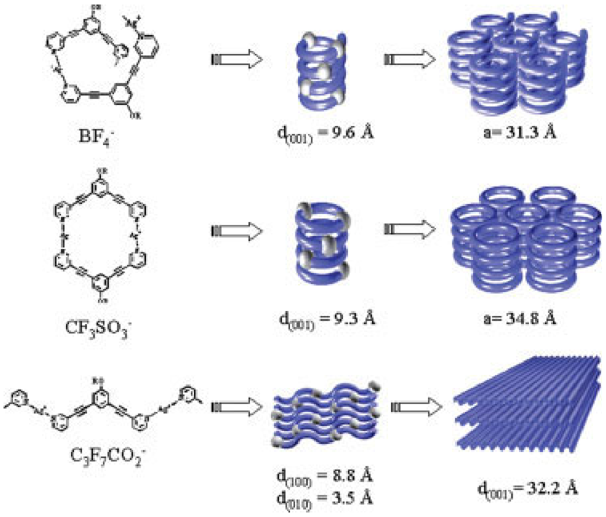

Figure 9. Schematic represenation of the self-assembly of coordination polymers and their subsequent self-organization. Reproduced from ref. 37, with permission from American Chemical Society (2004).

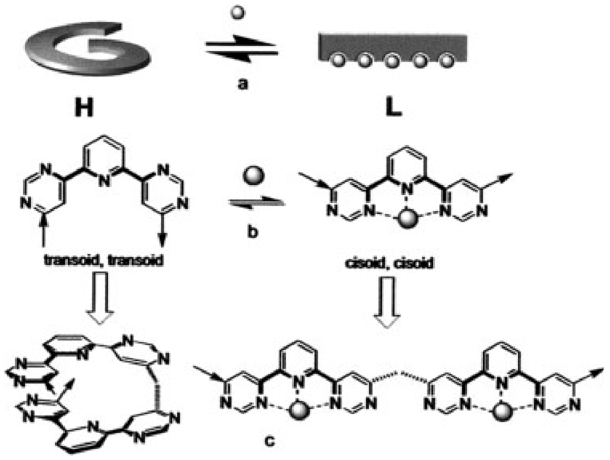

Figure 10. Ionic modulation of extension/contraction motions interconverting the helical free ligand and the extended linear multinuclear complex. Reproduced from ref. 68, with permission from the National Academy of Sciences (2002).

butyrate, organizes into a lamellar structure. The size of the BF_4^- ion is compatible with the internal cavity formed by the helical conformation of the ligands, indicating that the helical polymers can be constructed by tuning in the size of the counteranion.

REVERSIBLE CONFORMATIONAL CHANGES IN HELICAL STRUCTURES

Considerable efforts have recently been focused on the development of supramolecular helical polymers that undergo dynamic structural changes induced by internal or external stimuli.[63–65] A reversible folding/unfolding of helical conformation driven by a protonation reaction was recently introduced by Lehn and coworkers.[66,67] As aforementioned (Fig. 3),[56] the pyridine based oligoamide strand adopt stable helical conformations driven by the bending of the strands and are stabilized both by intramolecular hydrogen bonds between 2,6-bis(carbonylamino) pyridine units and 2,6-pyridinedicarboxamide units. Its crystal structure showed that the oligoamides fold into a helical conformation presenting three turns with π-stacking of pyridine rings (3.5 Å separation) and an average diameter of internal cavity was about 4 Å. When oligoamide was treated with triflic acid, regiose-

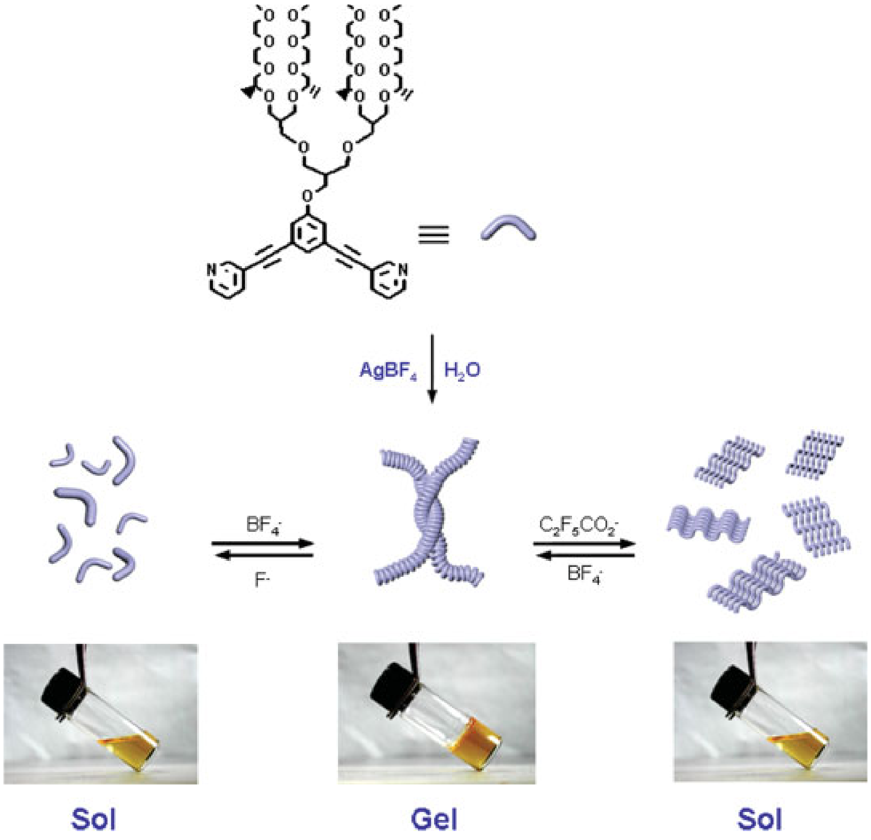

Figure 11. Schematic representation of reversible polymerization and reversible conversion between folded and unfolded conformations of a coordination chain upon counteranion exchange. Reproduced from ref. 69, with permission from Wiley (2005).

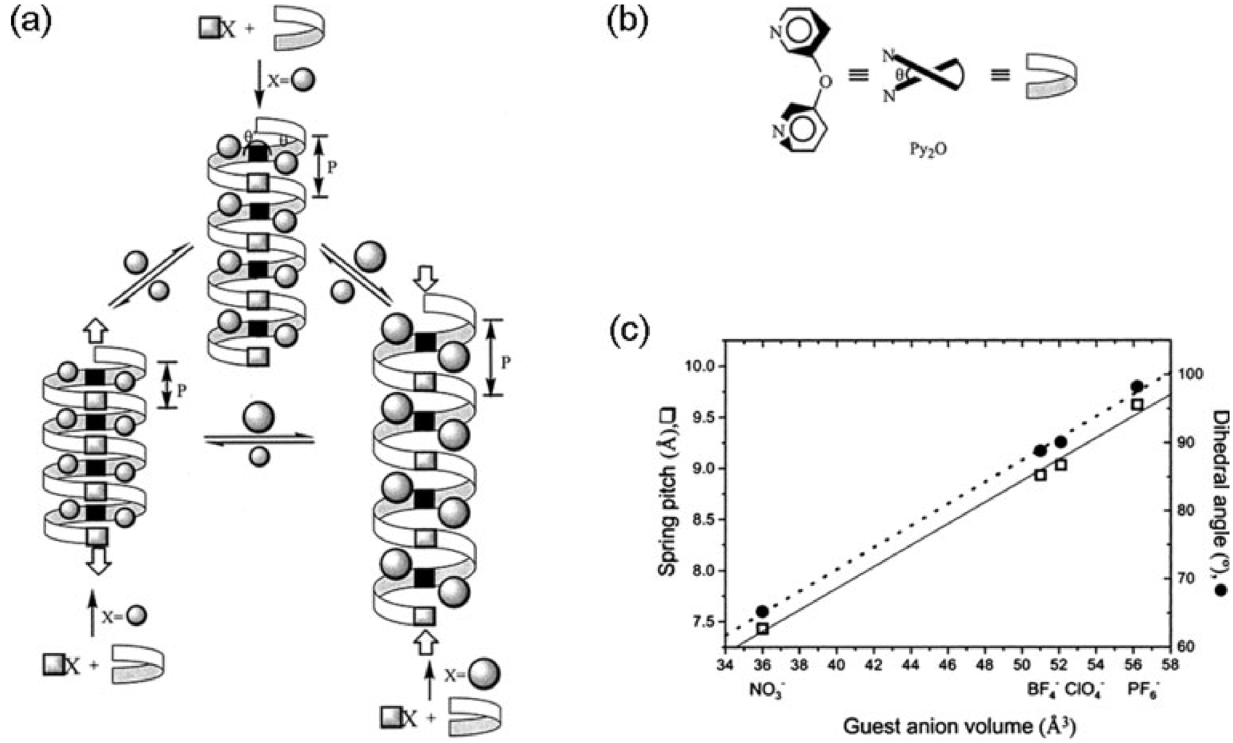

Figure 12. (a) Schematic representation and (b) molecular structure of the stable skewed conformational Py_2O and Ag(I) complex and (c) plot of the spring-pitch (Å) and the dihedral angle (°) as a function of the guest (X) volume in $[Ag(Py_2O)]X$ ($X^- = NO_3^-$, BF_4^-, ClO_4^-, and PF_6^-). Reproduced from ref. 70, with permission from American Chemical Society (2000).

lective protonation at the pyridine nitrogens of the 2,6-diaminopyridine and the subsequent rearrangement of the hydrogen bond induced unfolding of helical strand as confirmed by the crystal structure and 2D NMR. In another example, the helical structures of heterocyclic oligomers were shown to be interconverted between the coiled and uncoiled states, generating large amplitude ion-triggered molecular motions (Fig. 10).[68] The oligoheterocyclic strands consisting of alternating pyridine (py) and pyrimidine (pym) subunits connected in α-α′ positions would normally be extended into transoid/transoid strand of helical conformation. However, tridentate metal ion (Pb) coordination converts the transoid/transoid form of the free ligand to the cisoid/cisoid form of linear conformation.

Anion exchange can induce a conformational change of metal-coordinated helical polymers. Through the exchange of counteranions, our group has interconvert the secondary structure of cationic coordination chains in aqueous solution from a folded helical conformation into an unfolded zigzag conformation to exhibit a reversible sol–gel transition (Fig. 11).[69] As aforementioned, polymer based on BF_4^- anion adopts a folded conformation (Fig. 9).[37] These helical polymer aggregates into regular bundles of fibers, which get tangled up with each other to form an interwoven, 3D entangled network, and this behavior leads to the formation of gels. If a fluoride salt is added to the gel of helix, it rapidly liquefies. This is a result of the strong attraction of the fluoride ions (F^-) for the silver ions, which induce the depolymerizaion of helical polymer into individual molecules. More importantly, the gels reversibly transform into a fluid solution when counterion BF_4^- is exchanged with a larger ion, $C_2F_5CO_2^-$. When salts containing the $C_2F_5CO_2^-$ ion are added to the gel, it also liquefies. This reversible sol–gel transition results from the transformation of chain conformation into a translike layers as confirmed by TEM and fluorescence measurements.

SUPRAMOLECULAR SPRINGS

Jung et al. reported metal-coordinated helix as tunable spring that is reversibly operated by a counteranion exchange (Fig. 12).[70] In this helix, the skewed conformational 3,3′-oxybispyridine (Py_2O) as a helical component are connected through a complexation with the linear directional silver(I) ions. X-ray crystallographic

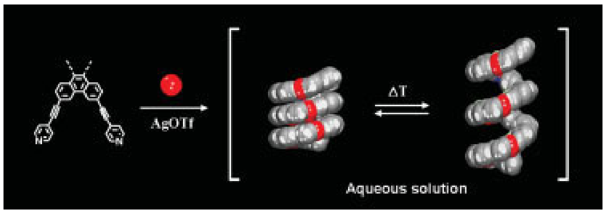

Figure 13. Schematic representation of a reversible helical spring. Reproduced from ref. 71, with American Chemical Society (2007).

characterization reveals infinite cylindrical helices which consist of a single strand of alternating Ag(I) and Py_2O, and there are two of these units in each turn. Interestingly, the counteranions are pinched in two columns between/inside the helical pitch, due to the presence of the weak electrostatic interactions between the Ag(I) cations and their counteranions. As a result, the single crystal structures of helical spring prepared by counteranion series (NO_3^-, BF_4^-, ClO_4^-, and PF_6^-) showed that each helical pitch is proportional to the volume of the counteranion guest within the flexible pitch-range (7.430–9.621 Å). The liability of the counteranions allows their replacement by other anions. The counteranion exchange experiment showed that the helix could be reversibly tuned as spring without destructing the skeleton within the flexible pitch-range. This spring motion was monitored by the characteristic IR bands of counteranions and powder XRD of skeleton backbone.

Similar to this tunable spring described earlier, the coordination supramolecular springs with switchable pitch can be achieved by temperature variation (Fig. 13).[71] In aqueous solution, this helical polymers are stabilized by π-stacked aromatic interactions (pyridine and phenanthrene units) surrounded by dendritic ethylene oxide chains. Above certain transition temperature, the absorption and CD spectra in chromophore regions, were red-shifted, which are attributed to elongated conjugation length, thus indicating extension of helix. These results can be explained by considering a lower critical solution temperature (LCST) behavior of the ethylene oxide chains in aqueous medium. Above the LCST, the ethylene oxide chains would be dehydrated to collapse into a molecular globule because of the loss of the hydrogen bonding between ether oxygens and water molecules. Consequently, the conformational transformation of the side ethylene oxide dendritic chains into a dehydrated molecular globule drives the π-stacked helical structure to be unstable due to steric crowdings between the globules with greater cross-sectional area. To relieve the steric crowdings at the interface, the helical strands would be extended to allow a larger interfacial area, thus lowering total free energy, as evidence by TEM and NMR.

CONCLUSIONS

This article highlights recent advancement in the formation of helical conformations in supramolecular systems and their stimuli-responsive conformational changes. Since the supramolecular helix conformations are critically dependent on the structures of the self-assembling molecules and the intricate balances in noncovalent interactions, many parameters should be considered in designing supramolecular helices. Helical organization in synthetic self-assembling systems can be achieved by a variety of strategies including intramolecular hydrogen bonding, solvophobic effects, and metal-ligand interactions. More interestingly, an alteration in the strength and configuration of the intra- and intermolecular noncovalent bonds can result in dynamic conformational transformation of the supramolecular helical structure, which eventually induces significant changes in the properties of the material. It is expected that such dynamic supramolecular responsive materials should find intriguing potentials to be used for dynamic nanodevices, optical modulators, and smart materials.

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