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Spontaneously Aggregated Chiral Nanostructures from Achiral Tripod−Terpyridine

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A chiral tripod−terpyridine ligand is known to coordinate with Ag^+. These complexes self-assemble into chiral aggregates at room temperature. Molecular dynamic simulation reveals the cooperation of tripodal ligand structures with Ag(I) cations, which leads to the formation of helical aggregations, thus the chirality.

1. Introduction

Recently, continuous attention has been paid to the chirality of supramolecular systems,[1] because of their important roles in both life and material sciences.[2] In general, the chirality of supramolecules may be achieved by the following two strategies: (a) at least one component is asymmetric or (b) the interaction between achiral components is dissymmetric, yielding a chiral association.[3] As one of the most known coordination systems, successful assemblies of metal−oligopyridine helices from chiral ligands[4] have been well studied. Actually, construction of chiral supramolecular assemblies from achiral components is even more interesting since macroscopic chirality could be realized by a stereoregular arrangement without any chiral auxiliaries, where molecular configuration plays crucial roles.[5] Study on molecules design and formation mechanisms of chirality is thus crucial for constructing novel and controllable superhelix especially from an achiral molecule.

We designed and synthesized a novel achiral tripod−terpyridine ligand, in which three terpyridine components were introduced into respective sites of silicon core to form tripodal configuration (Figure 1). The silicon core was selected because of increased interests in organosilicon chemistry and silicometallic chemistry in recent years.[6] The special conformation of the ligand (abbreviated as "L"), together with strong coordination ability of terpyridine unit with metals are expected to bring novel and diversified supramolecular architectures. Here, we report the unique formation of spontaneous chiral supramolecules and detailed theoretical calculations explain clearly the formation mechanism. Importantly, we are first successful for calculation the formation of large scale helical structures of organic aggregation.

2. Experimental Methods

General Information. Most of the chemical reagents were purchased from Acros or Aldrich Corporation and utilized as received unless indicated otherwise. All of the solvents were purified using the standard procedure. Column chromatograph was performed on neutral Al_2O_3. UV/vis spectra were recorded on a Jasco V-570 spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker Avance DPS-400 (400 MHz) spectrometer. MALDI-TOF mass spectrometric measurements were performed on Bruker Biflex MALDI-TOF. Circular dichroism (CD) spectra were conducted on a JASCO J-810 spectrophotometer. The bandwidth of CD beam is 4 nm, response was kept as 1 s, and sensitivity was kept as medium. The microscope was filled with nitrogen gas of high purity during the whole analytical process. Scanning electron micrographs (SEM) measurement and EDX spectra were performed with a JSM 6700 F NT equipped with a Link analytical system. The electron energy used was 20 keV. Atomic force microscopy measurements were carried out in air at room temperature with a Nanoscope instrument (digital instruments) operating in the tapping mode. Materials Studio package is used to carry out the model and the molecular dynamics (MD) simulation is run based on the PCFF force field.

Prepration of the Ligand.[7] *n*-Butyllithium (2.93 M in hexane, 0.5 mL, 1.5 mmol) was added dropwise to a dry THF solution (15 mL) of 4′-(*p*-bromophenyl)-2,2′:6′,2′′-terpyridine (388 mg, 1.5 mmol) under N_2 at −78 °C. The reaction mixture was further stirred for 10 min. Phenyltrichlorosilian (0.5 mmol, 105 mg) in 1 mL THF was added dropwise to the solution. The solution was gradually allowed to warm up to room temperature with stirring for 2 h. The reaction was then quenched by 0.5 mL water. The solvent was removed under reduced pressure and the product was isolated by flash column chromatography (neutral Al_2O_3, CH_2Cl_2 as eluent). Yield: 48% (245 mg). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 8.75−8.67 (m, 18H, Ha, Hd, He), 7.92−7.86 (m, 12H, Hg, Hf), 7.79−7.77 (d, 1H, Hj), 7.65−7.63 (d, 1H, Hj), 7.53−7.50 (t, 6H, Hc), 7.47−7.44 (t, 3H, Hh, Hi), 7.37−7.34 (t, 6H, Hb). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 156.1, 155.7, 150.2, 148.9, 138.3, 136.7, 131.9, 128.8, 128.7, 127.2, 123.7, 123.6, 121.2, 118.8, 118.7. MS (MALDI-TOF): 1027.50.

3. Results and Discussion

The ligand was synthesized by the reaction of 4′-(*p*-bromophenyl)-2,2′:6′,2′′-terpyridine with $PhSiCl_3$.[7] ^1H NMR, ^{13}C NMR, and MS (MALDI-TOF) results demonstrated that three Cl atoms in $PhSiCl_3$ were replaced by terpyridine units respectively, forming tripodal $PhSi(ttp)_3$. The coordination supramolecules were easily obtained by interfacial reactions of carefully spreading an aqueous solution of $AgNO_3$ (20 mg

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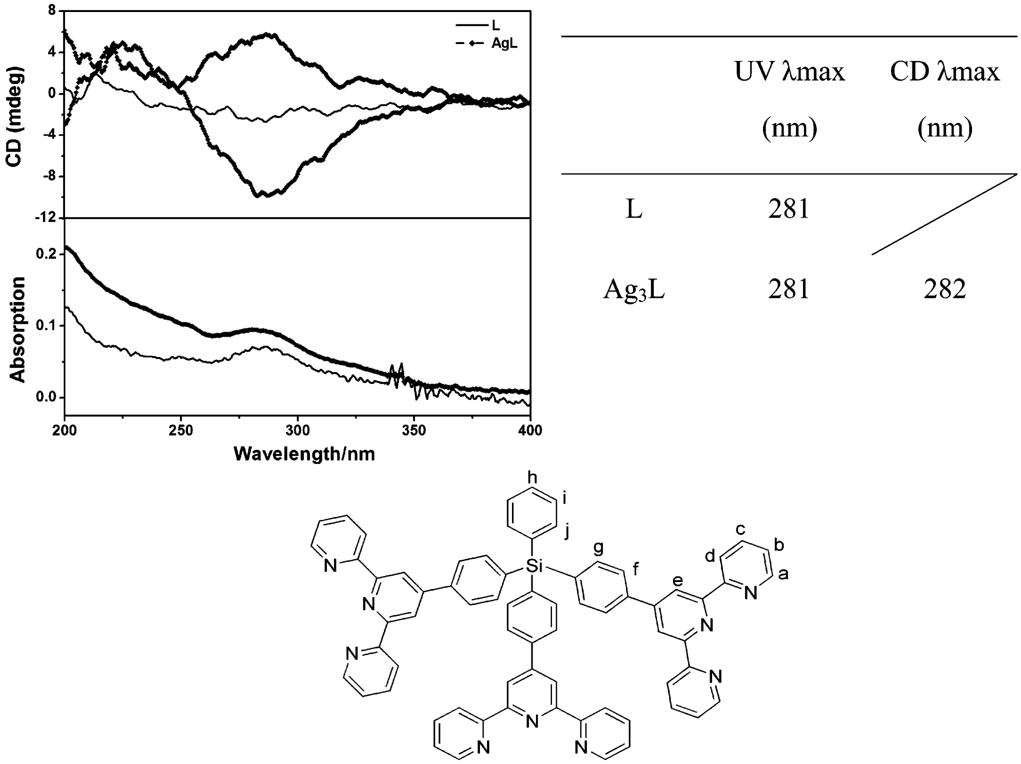

	UV λmax (nm)	CD λmax (nm)
L	281	
Ag_3L	281	282

Figure 1. UV/vis and CD spectra of the ligand and supramolecule $[AgL]_\infty$ on fused silica substrate (top). Molecular structure of the tripodal ligand L (bottom).

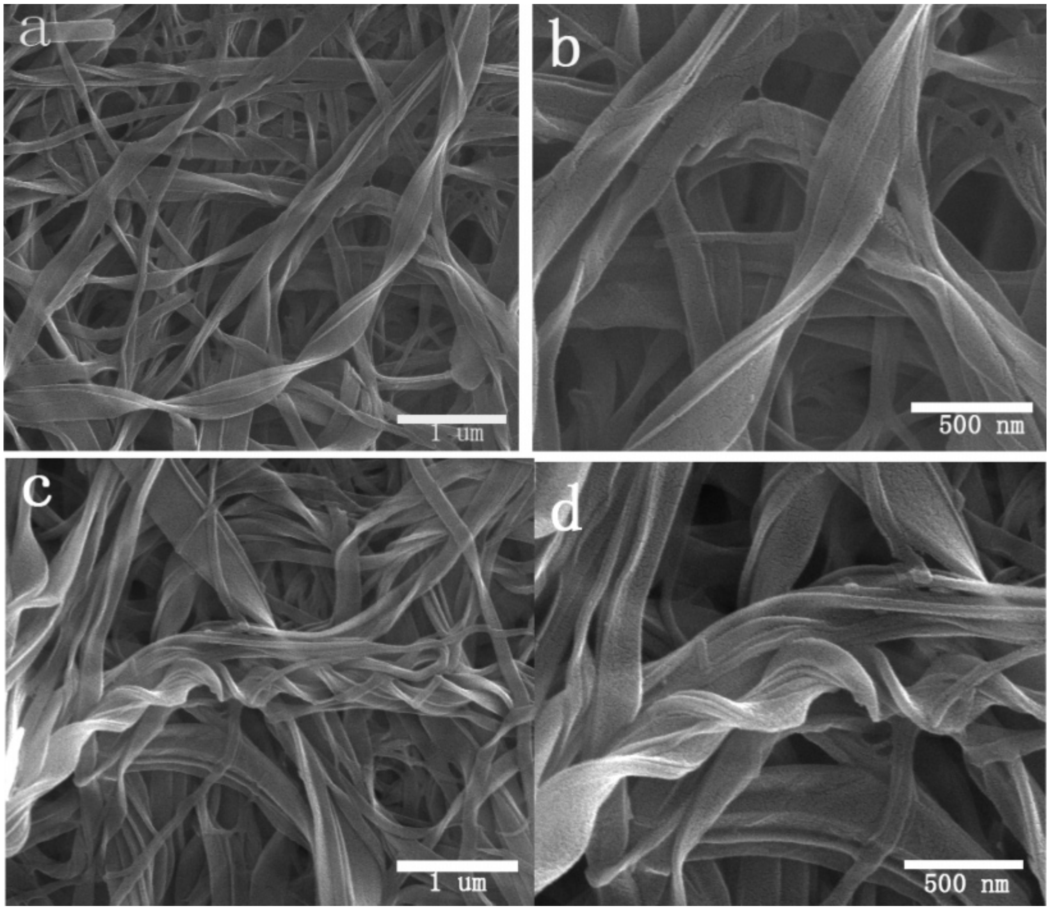

Figure 2. SEM (on Pt substrate) images of helical strips of $[Ag_3L]_\infty$ in different views and magnitude.

mL^{-1}) on a dichloromethane solution of the ligand (1 mg mL^{-1}).[8] The reaction was kept at room temperature for half an hour, and visible polymeric film formed at the interface. The films were carefully fished out with respective cleaned Pt and

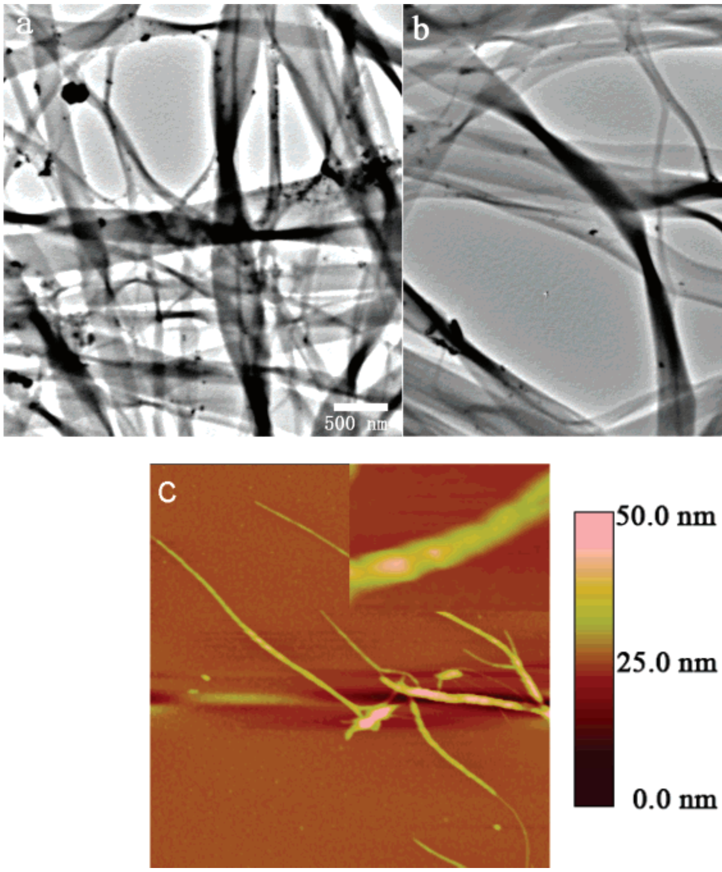

Figure 3. TEM (a, b, on copper grid) and AFM (c, 3.5 um × 3.5 um on mica) images of helical strips of **[**Ag_3L**]**$_\infty$. Magnified image shown in inset window (c, 440 nm × 320 nm).

fused silica substrates and rinsed by water and dichloromethane to remove no-reactive salts and ligands. The film was dried at room temperature under vacuum for 1 h before further measurements.

Figure 1 shows the UV−vis and circular dichroism (CD) spectra of the monomer ligand and formed supramolcule [AgL]$_\infty$. Both monomer and **[**AgL]$_\infty$ complex in film exhibit maximum absorption peak at 281 nm. The [AgL]$_\infty$ film was subjected to CD measurement, and it was interesting to note that [AgL]$_\infty$ film showed obvious chirality with cotton effect ($\lambda = 282$ nm), although the monomer ligand itself is achiral. It should be pointed out that both positive and negative cotton effects are obtained respectively on different spots of the same sample.

To elucidate the chirality of [AgL]$_\infty$ film, we performed scanning electron microscopy (SEM) measurement. Figure 2 show SEM pictures of [AgL]$_\infty$ film, where strips twisted in a right- or left-hand helix, with indefinite helical pitch. The width of these strips is ranging from 100 to 500 nm. SEM-EDX elemental analysis showed the molar ratio of Si:Ag:N atoms of the helical structure was approximately 1.00:3.73:10.04. Excessive molar ratio of N atoms than that in the ligand (9%) demonstrates the existence of counterion NO_3^- anions. There will be trace free NO_3^- ions from $AgNO_3$ in the subphase of the aggregation, supramolecular configuration is thus estimated **[**Ag_3L**]** complex.[9] According to previous reports on Ag complexes of pyridine ligands,[10] we consider that the observed helical structure is derived from cooperation of rigid tripodal skeleton of the ligand and its unique association mode with Ag cations. The coordination units tilted with respect to the local layer normal and the favored spirals from neighbor to neighbor leads the whole strip to twist into a superhelix.[11] The helical strips are also demonstrated by TEM (Figure 3a,b) and AFM (Figure 3c) images, which are in good accordance with the SEM picture. AFM measurements showed the thickness of single strand was about 30−40 nm. It should be pointed out that the AFM results represent finer helical features in comparison with those of SEM and TEM. Since the mechanisms and correction methods of such three micrograph techniques are different,[12−14] it is reasonable that images on differential scales are obtained. In principle, TEM and SEM results are more reliable and AFM technique can provide higher resolution.[12−14]

To clarify such a coordination complex formed at the interface quantitatively, X-ray photoelectron spectrum was performed. The binding energies were observed at 284.6 (C 1s), 406.0 (N, 1s), 399.2 (N, 1s), 532.0 (O, 1s), Si (101.7, 2p), and 367.75 eV (Ag, $3d^5$), respectively. The binding energy of 406.0 eV was attributed to N atoms in NO_3^- ions and 399.2 eV in C═N bonds.[9] Quantitative analysis shows the composition of Ag/Si is 3.27, which is similar to SEM-EDX results. FT-IR spectra also clarified the supramolecular configurations. The absorption bands at 1605, 1584, 1567 and 1548 cm^{-1}, which are assigned to the C═N stretching vibrations of the free ligand, are shifted to 1601 cm^{-1} center with broad absorption. This is consistent with the coordination of transition metals to nitrogen atoms.[15]

Materials Studio package from Accelrys[16] was used to carry out the model. The molecular dynamics (MD) simulation was run based on the PCFF force field and an energy minimization is performed. The MD simulation is done in NVT ensemble with a time step of 1.0 fs. Velocity Verlet integration method is used in the MD simulation. Temperature is set at 300 K, and the Andersen thermostat is used. Total number of MD steps is

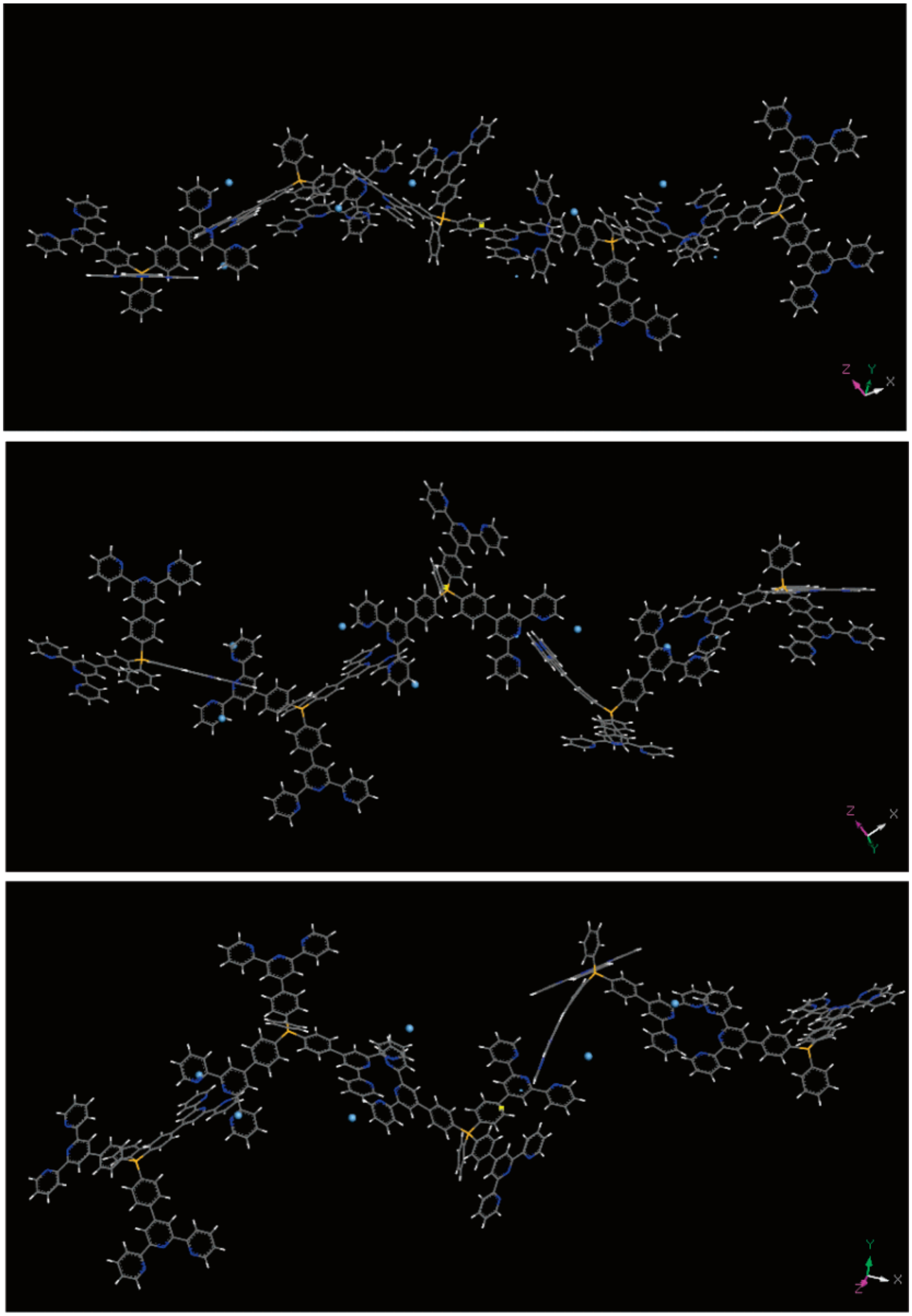

Figure 4. Different views of molecular configurations. Yellow and cyan spheres stand for silicon and silver cations, respectively.

5000. Different views of molecular configurations after a short MD relaxation are shown in Figures 4 and 5. From the configuration, it was obvious that only one of the bonds around silicon core was attached by a benzene cycle which resulted in breaking up of symmetry. The most preferred growing direction would be along or close to the benzene plane. The MD simulations demonstrated that two neighboring terpyridine molecules tend to form a unit by two biting jaws, which would be perpendicular to each other without silver ions. However, the introductions of silver ions fix the neighboring terpyridine planes in a tilt degree and make the plane deviate from the perpendicularity to a lower-energy conformation (Figure 6). The thermally stable assembly module from MD simulation indicates the tilted coordination between the terpyridine units with Ag cation could compensate the energy loss, as shown in the Figure 7. The energy loss from the optimized configuration to the initial geometry is about 4600 kcal/mol (5 units). The distance from Ag cation to

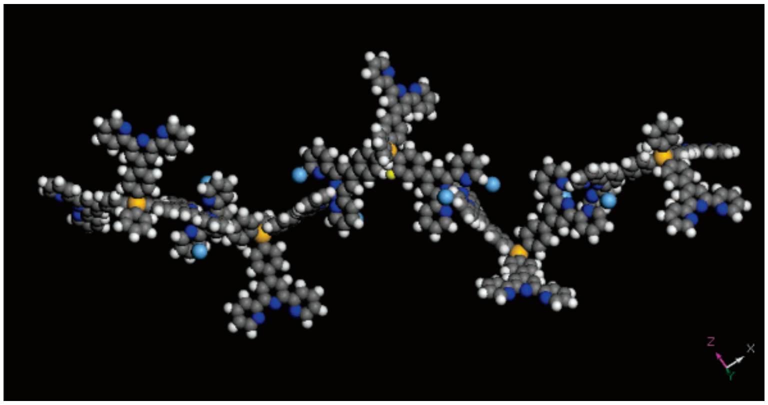

Figure 5. Initial molecular configuration. Yellow and cyan spheres stand for silicon and silver cations, respectively.

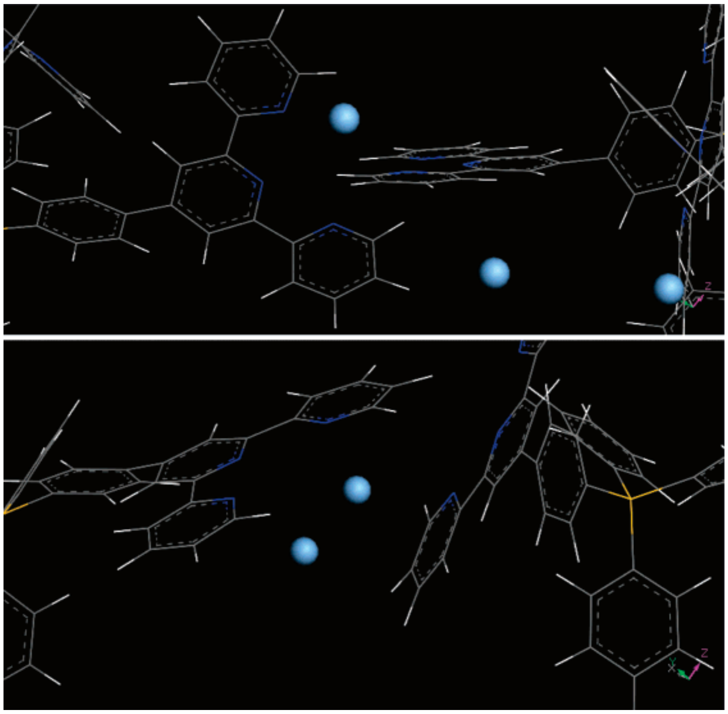

Figure 6. Enlarged views of two typical configurations of silver ions with terpyridines. Yellow spheres stand for silicon atoms, cyan spheres for silver ions. Blue lines represent terpyridine parts.

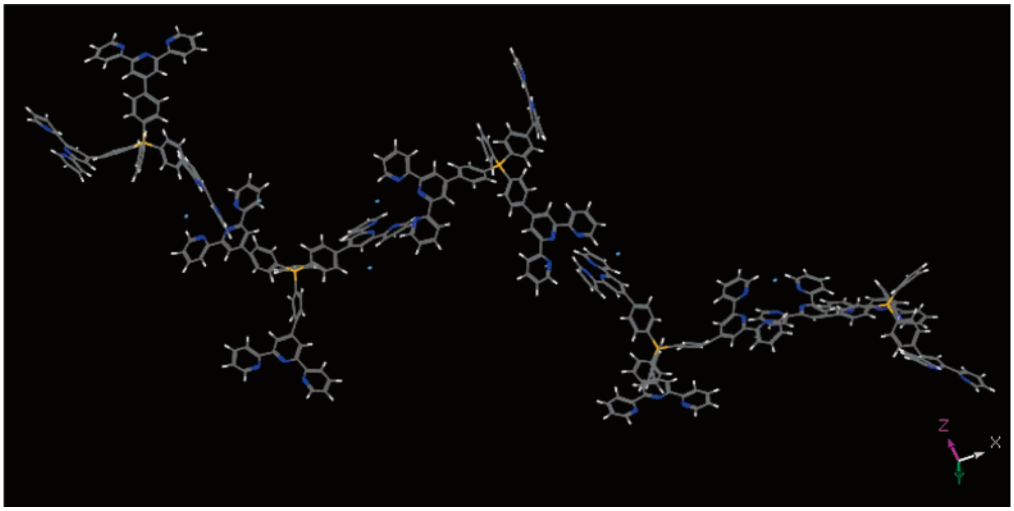

Figure 7. Thermally stable configuration after MD run in NVT ensemble.

coordinated terpyridine plane is about 3.2 Å. The energy loss for each Ag cation from coordinated to free state is about 4.4 kcal/mol. The MD results show that the tripodal terpyridine tends to grow in a spiraling style with the addition of silver ions, which leads the aggregation to a helical arrangement. The formation mechanism was thus proposed as shown in Figure 8.

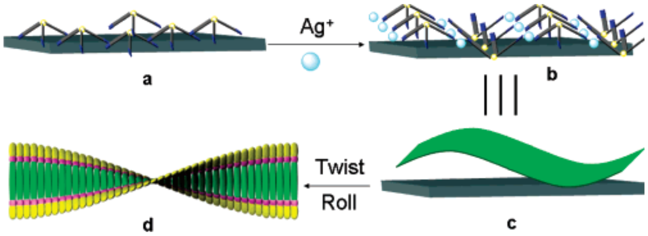

Figure 8. Proposed formation mechanism of the superhelix: free ligand molecules in dichloromethane (a), original flat strips with Ag cations (b, c), and twisted strips induced by continuous tilt of coordination planes between ligand and Ag cations. Yellow and cyan spheres represented silicon and Ag cations, respectively. Dark blue lines stand for terpyridine parts.

Flat strips were considered to form in the first stage, which have been demonstrated both in experiments and theories.[11,17] This was also verified by SEM and TEM images in our case. Due to the compression between ligands with Ag cations, these intermediate flat strips can further twist and roll into the helical structures.

4. Conclusions

In conclusion, chiral coordination architectures were constructed by self-assembly of an achiral tripod-ligand with silver(I) cations. The aggregation behavior and formation mechanism were discussed based on theoretical calculations. This work demonstrates an effective approach of designing ligand of specific configuration to study the effect of “structure−property” in molecular recognition process.

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