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Regulation of the Chiral Twist and Supramolecular Chirality in Co-Assemblies of Amphiphilic L-Glutamic Acid with Bipyridines

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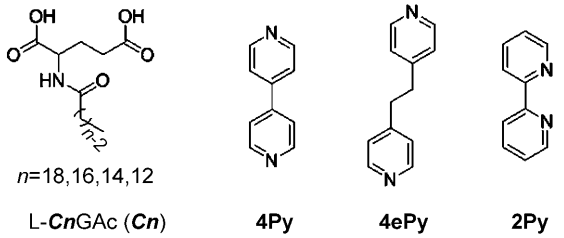
Abstract: A series of amphiphilic L-glutamic acid derivatives with various saturated alkyl chains has been designed and their co-assembly with 4,4′-bipyridine in aqueous media has been investigated. While the individual amphiphiles formed hydrogels with water and self-assembled into fine fiber networks, the addition of 4,4′-bipyridine caused significant changes in the co-assembled nanostructures such that twisted chiral ribbons were formed. In these supramolecular systems, either fine structural changes or adjustment of the stoichiometric ratio of the two components had crucial effects on the formation of the chiral twists. Based on detailed investigations by SEM and XRD analyses, FTIR, CD, and UV/Vis spectroscopies, and molecular simulation, it is considered that a delicate synergistic balance between π–π stacking, hydrophobic, and chiral interactions is responsible for the formation of the chiral twists. An interesting sandwich structure, in which an excess of 4,4′-bipyridine is inserted into the space of primary cages constructed from the amphiphile and 4,4′-bipyridine, is proposed. Remarkably, the handedness of these chiral twists is related not only to the chiral center of the glutamic unit, but also the chain length of the alkyl tails. This work provides a deeper understanding of the formation mechanism of chiral twists, and exemplifies a feasible shortcut to the rational design of chiral structures from basic molecular structures to supramolecular systems.

Keywords: amphiphiles · chirality · hydrogels · nanostructures · supramolecular chemistry

Introduction

Chiral structures such as helices and twists are among the most fascinating morphologies with geometrical asymmetry, which could store genetic information and be used as potential materials for chirotechnology.[1] It is an important issue in supramolecular chemistry to mimic these chiral structures and to obtain a comprehensive understanding of the mechanism of their formation.[2] The creation of artificial helical structures in relation to molecular design and controlled self-assembly have been extensively investigated.[3] For example, Lehn et al. have designed inorganic double-stranded helicates through the self-organization of oligobipyridine ligands with Cu^+ ions.[3a,b] Meijer et al. have created a helical polymer using the self-recognition of hydrogen bonds in a bifunctional monomer.[3c,d] Yashima et al. have synthesized complementary double helices utilizing interstrand amidinium carboxylate salt bridges between two homopolymers.[3e,f] Chiral twists, which have a similar structure to helices but with different curvature, are also frequently found in supramolecular systems.[4] Several simple amphiphiles, such as salts of 12-hydroxystearic acid,[5a,b] glutamates,[5c,d] phospholipids,[5e,f] sugar-based lipids,[5g,h] chiral geminal amphiphiles,[4a,b,5i] and amphiphilic peptides,[1g,5j] have been used to fabricate chiral twists. Some π-conjugated building blocks have also proved effective for the construction of chiral twists with a molecular motif of rod–coil or coil–rod–coil, such as hexa-*peri*-hexabenzocoronene (HBC),[6a,b] oligophenylenevinylenes (OPVs),[6c–f] oligophenyleneethynlenes (OPEs),[6g] ALS (*A*romatic, *L*inker, *S*teroidal group),[6h,i] C_3-symmetrical[6j,k] or X-shaped[6l] π-conjugated molecules, and so on.[7] However, there remain many unknowns concerning the formation of chiral twists. In particular, it is still a challenge to regulate chiral twists through either morphological parameters or nanoscopic and macroscopic chiralities.[8] In this paper, we report the formation and regulation of a chiral twist using a two-component system[9] composed of a series of L-glutamic acid derivatives and bipyridines (Scheme 1).



Scheme 1. Molecular structures of L-*Cn*GAc (***Cn***) and bipyridines (***x*Py**).

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We have designed a series of amphiphiles based on L-glutamic acid with saturated fatty acid chains of different lengths (Scheme 1). These compounds can self-assemble into nanofibers in water, thus leading to hydrogels. Interestingly, upon adding bipyridine to the system, the nanostructures underwent exciting changes due to strong hydrogen bonding between the carboxylic acid and the pyridyl nitrogen atoms.[10] In particular, the addition of 4,4′-bipyridine caused the formation of a chiral twist. Moreover, by changing the ratio of 4,4′-bipyridine to the amphiphile as well as the chain length of the amphiphile, both the pitch and the chirality of the twist could be regulated. Based on detailed investigations by SEM and XRD analyses, as well as FTIR, CD, and UV/Vis spectroscopic observations, the mechanism of the twist formation has been clarified. It has emerged that cooperativity between hydrophobic interactions of the amphiphiles, π–π stacking of the aromatic bipyridine, and hydrogen bonds between the bipyridine and L-glutamic acid is essential for the formation of chiral twists. In addition, the alkyl chain plays a crucial role in regulating the chirality of the twists. That is to say, amphiphiles with a longer alkyl chain transferred the molecular chirality of the L-glutamic acid to the macroscopic chiral twist, whereas those with a shorter alkyl chain did not. Our results provide a comprehensive understanding of the formation of the chiral twist.

Results

Self-assembly of *Cn* and hydrogel formation: All of the ***Cn*** molecules were difficult to dissolve in water at room temperature. However, upon heating to the boiling point of water, coupled with intense ultrasonication, clear aqueous solutions of ***Cn*** could be obtained. After allowing each solution to cool naturally to room temperature, it became opalescent and sticky. When the test vial was inverted the mixture no longer flowed, indicating the formation of a hydrogel. Figure 1 shows SEM images of the xerogels obtained from air-dried ***Cn*** hydrogels. Worm-like nanofibers of several micrometers in length were formed and built up into three-dimensional (3D) networks, in which water molecules were trapped to form hydrogels (Figure 1a, inset).[11]

Co-assembly behaviors of *C18*/*x*Py: When ***C18*** was mixed with **4Py** in a molar ratio of 1:2, a white opaque hydrogel was formed. Interestingly, SEM and TEM observations of the nanostructures revealed beautiful twists with exclusively right-handedness rather than fine fibers, as shown in Figure 2. The twists were uniform with a pitch of around 2.80 μm and a width of 24–30 nm. Surprisingly, when either **4ePy** or **2Py** was mixed with ***C18***, only precipitates were obtained. In these cases, the mixtures of ***C18*** and bipyridines also formed an organized nanostructure, which appeared as nanotapes and nanoplates in the SEM images. This strongly suggested that the ***C18*** molecules could interact with all three ***x*Py** molecules, giving rise to distinct co-assembly behaviors according to the structural differences of ***x*Py**.

Effect of *C18*/*x*Py ratio on morphological evolution: In order to further probe the nature of the assembly of ***C18*/*x*Py**, we varied the mixing ratio. At all investigated stoichiometries of the ***C18*/4ePy** or ***C18*/2Py** mixtures, precipitates were invariably formed with the same nanoplates or nanotapes in their nanostructures (Figure 2d, e and Figure S1 in the Supporting Information). However, hydrogels were formed over a wide range of mixing ratios for ***C18*/4Py**. Interestingly, the self-assembled nanostructures were quite different. Figure 3 shows SEM images of various ***C18*/4Py** combinations. At ***C18*/4Py** = 1:1, flat ribbons were predominantly formed (Figure 3a). When a little more **4Py** was added, the ribbons started to twist (Figure 3b). On further increasing the amount of **4Py**, the twisted ribbons became more numerous and their pitch gradually became smaller (Figure 3c, d). Essentially uniform perfect twists were obtained at ***C18*/4Py** = 1:2 and remained unchanged up to a ratio of 1:3 (Figure 3e, f). In addition, the ***C18*/4Py** twists had exclusively

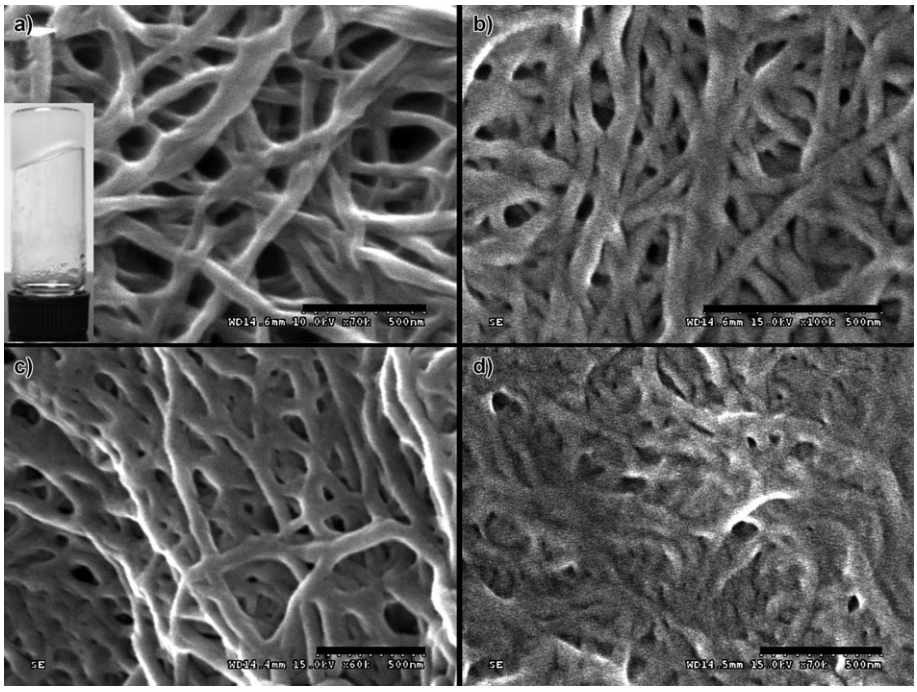

Figure 1. SEM images of ***Cn*** xerogels, ***C18*** (a), ***C16*** (b), ***C14*** (c), and ***C12*** (d). The inset is a photograph of the ***C18*** hydrogel. Scale bar: 500 nm.

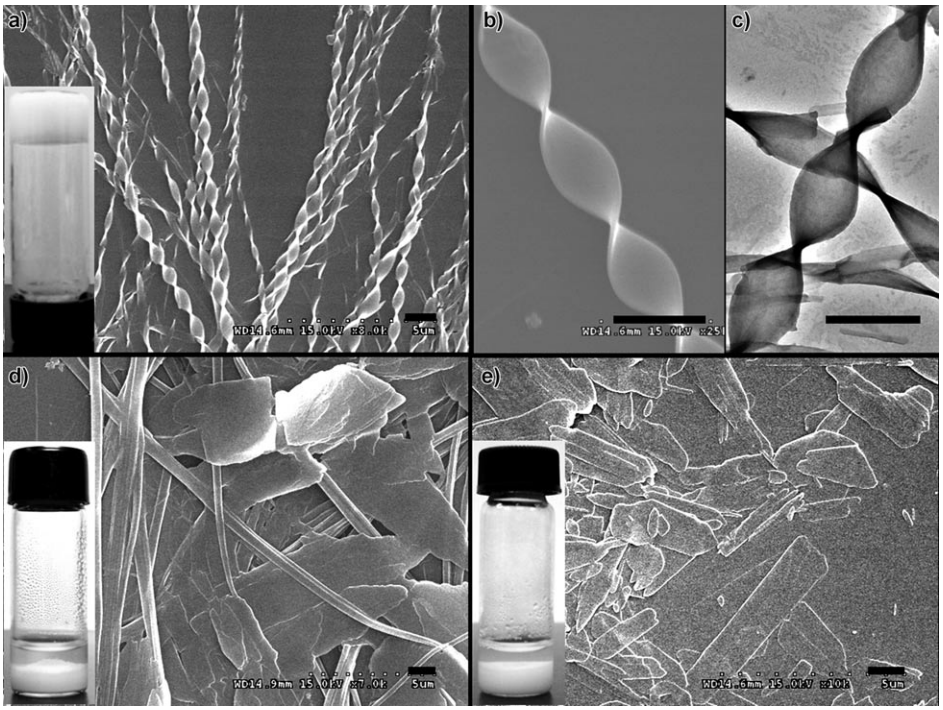

Figure 2. Morphologies of co-assembled ***C18*/4Py** (a, b, c), ***C18*/4ePy** (d), and ***C18*/2Py** (e) at molar ratios of 1:2. The insets are photographs of the samples. Scale bar: 1 μm.

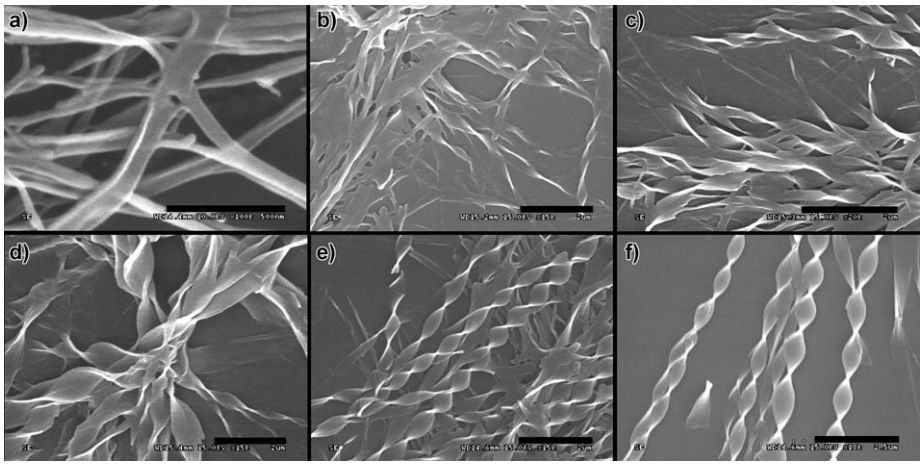

Figure 3. SEM images of co-assembled ***C18*/4Py** at different molar ratios, 1:1 (a), 1:1.2 (b), 1:1.5 (c), 1:1.8 (d), 1:2 (e), and 1:3 (f). Scale bar: 500 nm (a), 2 μm (b–f).

right-handedness, suggesting that this stemmed from the nature of the original molecular chirality.

Effect of the length of the *Cn* alkyl chain on the twists: Similar investigations were carried out for the other three amphiphiles ***Cn*** (***C16***, ***C14***, and ***C12***) with different bipyridines ***x*Py**. When these ***Cn*** were mixed with **4ePy** or **2Py**, almost the same nanoplates or nanosheets were observed as found for ***C18*/4ePy** or ***C18*/2Py**, regardless of the chain length of ***Cn*** or the ***Cn*/4ePy** or ***Cn*/2Py** ratio (Figures S2 and S3). In contrast, ***Cn*/4Py** formed hydrogels, the morphologies of which showed an interesting change depending on the chain length of the amphiphile ***Cn***. Figure 4 shows SEM images of ***Cn*/4Py** xerogels, which clearly show the different features.

Firstly, ***C16*/4Py** showed similar self-assembly behavior to that of ***C18*/4Py** (Figure 4a–c). That is to say, mainly nanoribbons were formed at ***C16*/4Py** = 1:1 while chiral twists were predominantly observed at 1:2, which remained unchanged up to 1:3. Moreover, the chirality of all of the twists retained the same right-handedness. Again, this suggested that the molecular chiral information of the amphiphile ***C16*** was transferred to the supramolecular assemblies of ***C16*/4Py** and amplified to the nanometer scale.[9e,10i]

Secondly, analogous twists were observed for all of the investigated ***C14*/4Py** combinations, including ***C14*/4Py** = 1:1. As denoted by the arrows in Figure 4d–f, both left- and right-handed twists were simultaneously observed in all ***C14*/4Py** mixtures, which is different from the exclusively right-handed twists of ***C18*/4Py** and ***C16*/4Py**. These surprising results were consistently obtained in several repeated experiments, which clearly indicated that the chiral nature of the molecules was not the only factor responsible for the chirality of the twists. Nanoscale twists of opposite handedness could be produced from the same chiral molecule.[8a–d]

Thirdly, in all of the ***C12*/4Py** mixtures, nanotapes composed of fine nanofibers were predominantly formed, with only a small amount of twists and helical fibers (Figure 4g–i). This further indicated that the alkyl chain length of amphiphiles ***Cn*** had a dramatic influence on the co-assembled nanostructures.

It should be noted that the pH of the aqueous solutions had a significant effect on the gel formation as well as the gel structures. It was found that neutral pH was favorable for twist formation. This might be due to the strong H-bonding between the carboxylic acid and the pyridine at neutral pH.[18c]

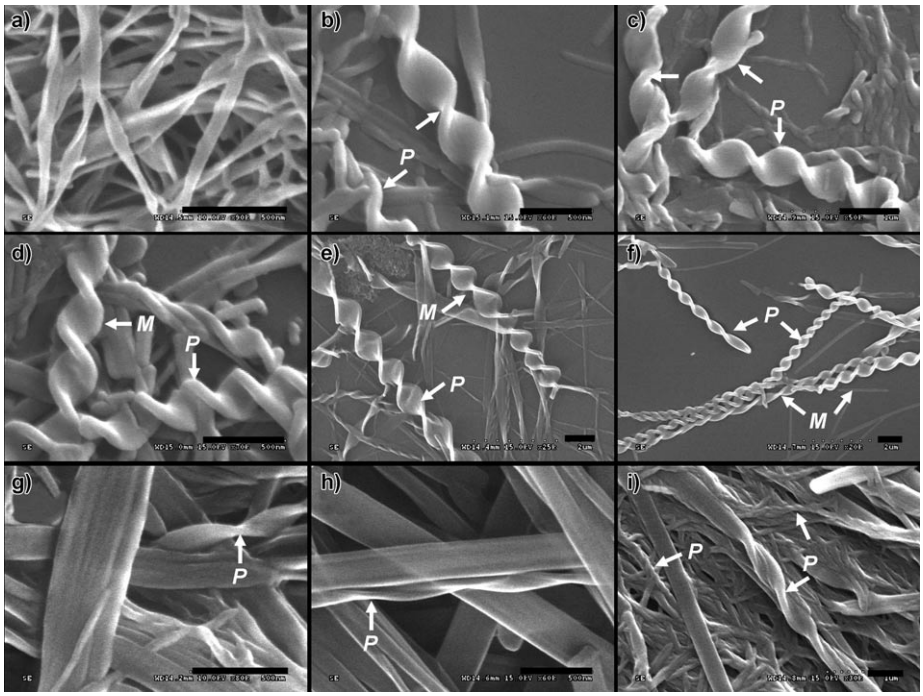

Figure 4. SEM images of co-assembled ***C16*/4Py** (a, b, c), ***C14*/4Py** (d, e, f), and ***C12*/4Py** (g, h, i) at different molar ratios, 1:1 (a, d, g), 1:2 (b, e, h), and 1:3 (c, f, i). Scale bar: 500 nm. The white arrow marks designate the chiral twists, and *M* and *P* denote the left- and right-handed twists, respectively.

FTIR spectra of the supramolecular assemblies: FTIR spectra were recorded to explore molecular interactions in the supramolecular assemblies. For the ***C18*** xerogel (Table 1 and Figure 5a), the occurrence of the amide I and amide II bands at 1645 and 1545 cm^{-1}, respectively, indicated that the amide groups formed strong hydrogen bonds.[12] Bands at 1731, 1694, and 1676 cm^{-1} suggested that the two carboxylic acid groups were also involved in various hydrogen bonds.[12b] Moreover, the appearance of two peaks due to N–H stretching vibrations at 3327 and 3310 cm^{-1} further evidenced the complicated nature of the hydrogen bonds. In addition, bands attributable to asymmetric and symmetric CH_2 stretching vibrations at 2918 and 2850 cm^{-1}, respectively, indicated that the alkyl chains were closely packed in a highly ordered fashion (all-*trans* zigzag conformations).[13]

The FTIR spectrum of the ***C18*/4Py** = 1:1 xerogel displayed two new strong vibrational bands at around 2500 and 1945 cm^{-1} (Table 1 and Figure S4a), which are typical of carboxylic acid–pyridine hydrogen-bond interactions.[10b,c,f,g] Such interaction is further evidenced by the shifts of the vibrational bands of C=N and C=C in the pyridyl rings from 1591 and 989 cm^{-1} to 1603 and 1005 cm^{-1}, respectively.[10b,d] This suggested that carboxylic acid–pyridine hydrogen bonds were formed between ***C18*** and **4Py**. Meanwhile, three vibrational bands at 1731, 1694, and 1676 cm^{-1} disappeared and only one band remained at 1729 cm^{-1}. This indicated that the carboxylic acid groups of ***C18*** that had previously been involved in diverse H-bonds now interacted exclusively with **4Py** due to the stronger carboxylic acid–pyridine hydrogen-bond interactions.[10b] However, the amide I and amide II bands at 1652 and 1546 cm^{-1} demonstrated that the hydrogen bonds between amide groups remained intact. The asymmetric and symmetric CH_2 stretching vibrations at 2917 and 2850 cm^{-1} indicated that the highly ordered structure of the alkyl chains was preserved upon mixing.

Table 1. Main vibrational bands [cm^{-1}] in the FTIR spectra of ***C18*** and ***C18*/*x*Py** assemblies.

Assignment	***C18***	***C18*/4Py**		***C18*/4ePy**		***C18*/2Py**	
		1:1	1:2	1:1	1:2	1:1	1:2
vNH	3327, 3310	3315	3315	3318	3317	3313	3312
vCH_2	2918	2917	2917	2917	2917	2917	2917
		2850	2850	2850	2850	2849	2850
vOH[a]	2850	2500	2499	2506	2495	2547	2525
		1945	1944	1947	1947	1940	1943
vC=O	1731	1729	1729	1733	1733	1745	1745
	1694, 1676					1715	1717
amide I	1645	1652	1652	1648	1648	1651	1652
vC=N[b]		1603	1603	1611	1609	1605	1605
			1592		1597	1589	1589
amide II	1545	1546	1543	1546	1543	1552	1552
$\delta(CH_2)_n$	1471	1470	1467	1472	1472	1472	1472
	1455			1464	1465	1463	1464
δC=C[c]		1005	1005	1019	1019	1007	1007
			990		992		

[a] Stretching vibration of the hydroxy group in carboxylic acid–pyridyl hydrogen bonds. [b] Stretching vibration of the pyridine ring. [c] Twisting vibration of the pyridine ring.

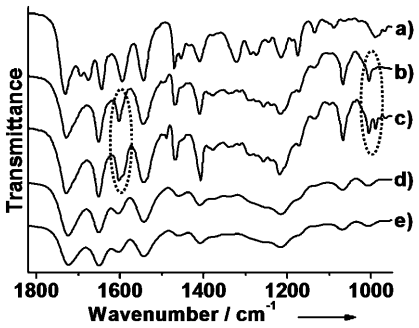

Figure 5. FTIR spectra of the xerogels, ***C18*** (a), ***C18*/4Py** = 1:1 (b), ***C18*/4Py** = 1:2 (c), ***C12*/4Py** = 1:1 (d), and ***C12*/4Py** = 1:2 (e).

The FTIR spectral changes seen for ***C18*/4ePy** = 1:1 were similar to those described above for ***C18*/4Py** = 1:1 (Table 1 and Figure S4b). Two new bands at 2506 and 1947 cm^{-1} (the stretching vibration of a pyridyl-bonded hydroxy group of the carboxylic acid function) and shifts in the bands at 1591 and 989 cm^{-1} to 1609 and 1019 cm^{-1} (the vibrations of the C=N and C=C of **4ePy**, respectively), suggested the formation of a H-bonded ***C18*/4ePy** complex with a similar supramolecular structure to that of ***C18*/4Py** = 1:1.

In contrast, the FTIR spectrum of ***C18*/2Py** = 1:1 featured two vibrational bands at 1745 and 1715 cm^{-1} in the relevant region for carboxylic acid functions, although two new bands at 2547 and 1940 cm^{-1} indicated the occurrence of the carboxylic acid–pyridine H-bond interaction (Table 1 and Figure S4c). This suggested a distinct interaction mode of ***C18*** with **2Py** compared to that with the former two pyridines. That is to say, one carboxylic acid group of ***C18*** formed an H-bond with **2Py** as in the case of **4Py** or **4ePy**, while the other was seemingly free in the ***C18*/2Py** complex.[12b]

As expected, the other ***Cn*** xerogels displayed FTIR spectra almost the same as that of ***C18***, except that the asymmetric and symmetric CH_2 stretching vibrations gradually shifted from 2918 and 2850 cm^{-1} (***C18***) to 2922 and 2852 cm^{-1} (***C12***), respectively, implying looser packing with shortening of the alkyl chains of ***Cn*** (Figure S4d and Table S1).[13]

For all of the ***Cn*/4Py** = 1:1 xerogels, the same vibrational bands at 2500, 1945, and 1729 cm^{-1} confirmed the formation of carboxylic acid–pyridine hydrogen bonds (Table S1).[10b] Significantly, these three bands remained unchanged, despite the dramatic morphological evolution upon changing the ***C18*/4Py** ratio from 1:1 to 1:2. However, remarkable differences were observed at lower vibrational frequencies. That is to say, the FTIR spectrum of the ***C18*/4Py** = 1:2 xerogel featured two minimally shifted bands (1592 and 990 cm^{-1}) from 1591 and 989 cm^{-1} for the C=N and C=C vibrations of the pyridine ring besides the two more significantly shifted bands at 1603 and 1005 cm^{-1} found for the ***C18*/4Py** = 1:1 xerogel[10b,d] (Figure 5b, c). Apparently, the two less shifted bands could be attributed to the vibrations of weakly bound **4Py** molecules. From these observations, we inferred that in the ***C18*/4Py** = 1:2 hydrogel, the redundant **4Py** is probably sandwiched into the space between the two **4Py** units of the primary ***C18*/4Py** = 1:1 complex. Such FTIR spectral changes were also obtained for the ***C16*/4Py** and ***C14*/4Py** xerogels when the ratio was changed from 1:1 to 1:2. However, the FTIR spectrum of ***C12*/4Py** = 1:2 was identical to that of the 1:1 xerogel (Figure 5d, e), possibly indicating that no sandwich structure akin to those formed with the three longer-chain amphiphiles was adopted in this case. Moreover, the shifts of the asymmetric and symmetric CH_2 stretching vibrations to 2922 and 2852 cm^{-1} for ***C12*/4Py**, as compared to 2918 and 2850 cm^{-1} in the other three cases, implied that the alkyl tails of ***C12*/4Py** were less tightly packed.[13] Comparing the UV/Vis spectra (Figure 7d, solid line), a 4 nm red shift of the maximum absorbance band of the ***C12*/4Py** hydrogel compared with that of an aqueous solution of **4Py** indicated proton transfer from the carboxylic acid group of ***C12*** to the pyridyl N atom of **4Py**. From these observations, we could infer that shortening of the alkyl chain led to an increase in the water-solubility of ***C12***. As a consequence, the weakened hydrophobic interaction and carboxylic acid–pyridine hydrogen bonds might be responsible for the fact that no sandwiched **4Py** and no twist formation were observed.

X-ray diffraction measurements on the supramolecular assemblies: X-ray diffraction measurement was also used to evaluate the nanostructures of the supramolecular assemblies. Figure 6 displays the XRD patterns of the xerogels of

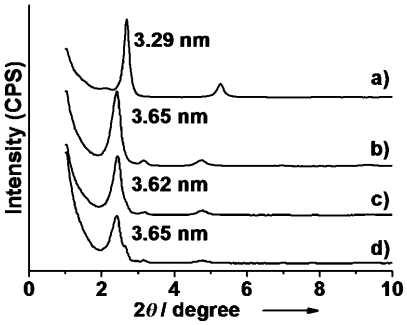

Figure 6. XRD spectra of the xerogels, ***C18*** (a), ***C18*/4Py** = 1:1 (b), ***C18*/4Py** = 1:2 (c), and ***C18*/4Py** = 1:3 (d).

pure ***C18*** and the composites ***C18*/4Py**. According to Bragg's equation, the *d*-spacing of the ***C18*** xerogel was estimated to be 3.29 nm, suggesting a bilayer structure formed by ***C18*** molecules.[12b] Well-defined patterns were also observed for the ***C18*/4Py** xerogels and the interlayer distance became larger (ca. 3.65 nm). This indicated that a composite bilayer was formed in which the **4Py** molecules were packed in an orderly manner between the ***C18*** molecules through carboxylic acid–pyridine interactions. Similar XRD results were obtained for all of the other combinations (Figure S5), suggesting that the basic unit of each of the nanostructures was a certain bilayer structure, regardless of whether nanotwists or nanosheets were formed.

Supramolecular chirality of the twists: SEM observation revealed the microscopic chirality of the twists. To further characterize their nanoscale chirality, circular dichroism (CD) spectra were measured. Even though the pure ***Cn*** molecules could aggregate into ordered nanofibers and subsequently form hydrogels, neither UV/Vis spectral activity nor CD activity was detected in the range 200–400 nm due to the lack of a chromophore (Figure S6d). Aqueous solutions of the three individual bipyridines ***x*Py** were UV/Vis spectrally active (**4Py**: 240, ca. 270 nm; **2Py**: 234, 281 nm; **4ePy**: ca. 250, 256, 263 nm) but CD silent due to their achiral nature (Figure 7, dotted line). For co-assembled ***C18*/*x*Py**, no remarkable changes in the UV/Vis spectra were ob-

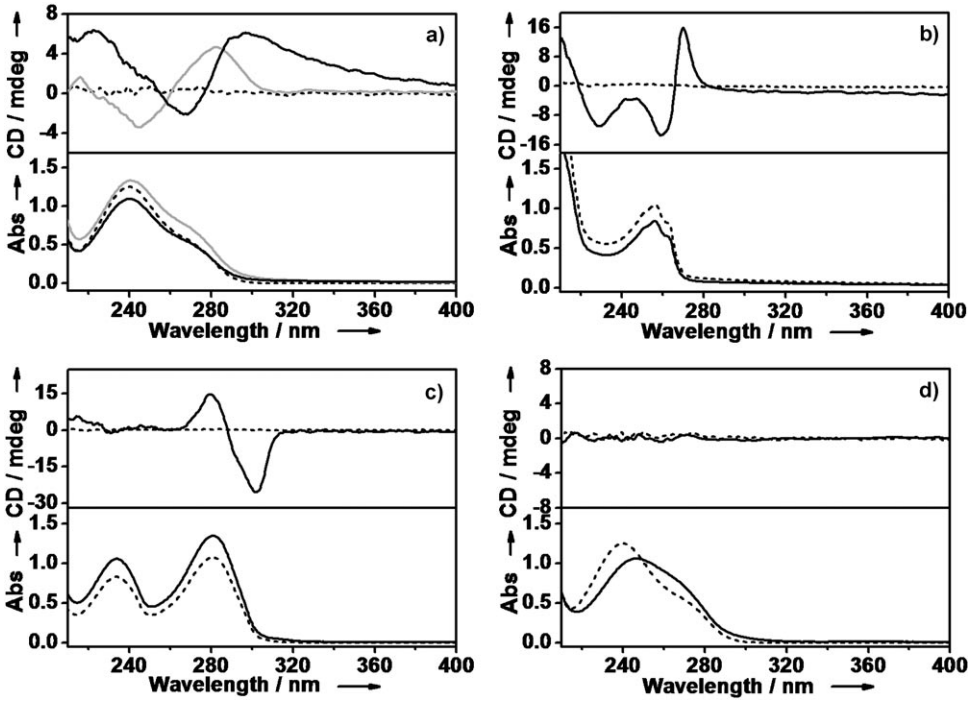

Figure 7. CD and UV/Vis spectra of ***C18*/4Py** (a, solid line), ***C16*/4Py** (a, gray solid line), ***C18*/4ePy** (b), ***C18*/2Py** (c), and ***C12*/4Py** (d) at molar ratios of 1:2, as well as those of aqueous solutions of pure ***x*Py** (dotted line), **4Py** (a), **2Py** (b), and **4ePy** (c).

served. However, significant CD signals were detected. Specifically, a strong positive Cotton effect was observed for the ***C18*/4Py** hydrogel with a crossover at 277 nm, which corresponded to the electronic transition of the **4Py** rings (Figure 7a, solid line). Also, a positive Cotton effect with a crossover at 285 nm was detected for ***C18*/4ePy**, whereas a negative Cotton effect with a crossover at 266 nm was found for ***C18*/2Py** (Figure 7b, c, solid lines). The strong CD activities observed for ***C18*/*x*Py** demonstrate that upon cooperative self-assembly, the molecular information of chiral ***C18*** was successfully transcribed to the achiral ***x*Py** chromophores.[9e,10i] Moreover, the opposite sign of the CD signals suggested a distinct chirality transcription mode for ***C18*/2Py** compared to that for ***C18*/4Py** or ***C18*/4ePy**.[11,m,9g] This further corroborated their different molecular interactions as revealed by the FTIR results.

Similarly, ***C16*/4Py** displayed a strong positive Cotton effect and the crossover appeared at 260 nm, a much lower wavelength compared to 277 nm for ***C18*/4Py** (Figure 7a, gray solid line). This suggested that the alkyl chain length of the amphiphiles could influence the aggregation behavior of the chromophores **4Py**. Even though ***C14*/4Py** displayed the same UV/Vis spectrum as ***C18*/4Py** and ***C16*/4Py**, it was CD silent owing to the coexistence of right- and left-handed twists (Figure S6c). The CD inactivity of ***C12*/4Py** may be a result of weaker carboxylic acid–pyridyl hydrogen-bonding interactions because of proton transfer from ***C12*** to **4Py**, as evidenced by a 4 nm red shift from 240 to 244 nm (Figure 7d, solid line). It would seem that strong carboxylic acid–pyridyl H-bonds play a pivotal role in chirality transcription.

Discussion

It was clear from the above results that the ***Cn*** amphiphiles could form hydrogels with **4Py**, but formed precipitates with **4ePy** or **2Py**. The two components self-assembled cooperatively to form various nanostructures such as fibers, ribbons, sheets, and twists. Moreover, the morphologies of the nanostructures could be tuned by varying the chain length of ***Cn***,[4b,5i,14] the chemical structure of ***x*Py**, and their stoichiometric ratio.[15] It was clear that multifarious noncovalent interactions were involved, such as carboxylic acid–pyridyl hydrogen bonds, amide–amide hydrogen bonds, aromatic π–π stacking, and alkyl hydrophobicities. Furthermore, it was suggested that the formation of chiral twists may be attributed to synergistic effects among these noncovalent interactions.

Each L-glutamic acid-based amphiphile ***Cn*** has three hydrogen-bond sites, that is, two carboxylic acid groups and one amide function, and as a result several types of carboxylic acid–carboxylic acid, carboxylic acid–amide, and amide–amide hydrogen bonds could be formed.[12b] Through hydrophobic interactions of their alkyl chains, the amphiphiles themselves first aggregate into a bilayer structure. These bilayer subunits are further stacked in a layer-by-layer fashion and then self-assemble into fibrils, which become intertwined to form nanofibers of diameter about 21 nm.[5g,16] Subsequently, the nanofibers become woven into 3D networks, which can trap water molecules, thereby leading to hydrogels (Figure S7).

When ***x*Py** was introduced, the self-recognizing carboxylic acid–pyridyl hydrogen bonds took priority over the primary carboxylic acid–carboxylic acid and carboxylic acid–amide hydrogen bonds of the ***Cn*** molecules. Therefore, supramolecular ***Cn*/*x*Py** was produced as the basic building block for further assembly (Figure 8 and Figure S8). FTIR spectra verified that carboxylic acid–pyridyl hydrogen bonds were predominantly formed instead of the diverse hydrogen bonds between carboxylic acids. However, the amide–amide hydrogen bonds were well preserved. Owing to the highly directional hydrogen bonds and the strong hydrophobic interactions between the alkyl chains, an ordered composite bilayer structure was formed. Compared with the bilayers

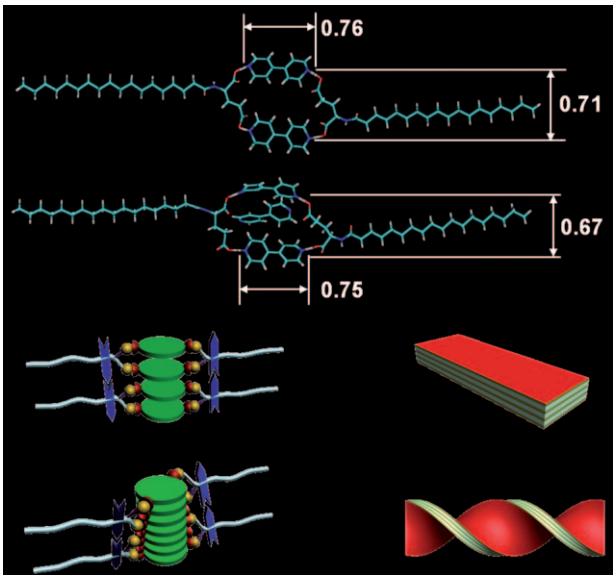

Figure 8. Model for the formation mechanism of a co-assembled chiral twist from ***C18*/4Py** (for details, see discussion text).

formed by the pure ***Cn*** molecules, the composite bilayers were further stabilized by additional π-π stacking interactions between the aromatic bipyridines ***x*Py**. This basic unit imparted the resulting bilayers with extra rigidity. As a result, flat ribbons were formed instead of worm-like fibers. At a 1:1 ratio of ***C18*/4Py**, the carboxylic acid and bipyridine combined to produce this structure and self-assembled into flat strips or ribbons due to the increased rigidity of the headgroups. When a slight excess of **4Py** was added, the flat ribbons started to twist because of the involvement of more π–π stacking interactions. Apparently, the additional **4Py** was inserted into the cavity. We have carried out a PCMODEL simulation on such a structure. It showed a remarkable decrease in the distance between the two intermolecular carboxylic groups of the ***C18*** molecule from 0.71 nm in ***C18*/4Py** = 1:1 to 0.67 nm in ***C18*/4Py** = 1:1.5. This result supports the view that when additional **4Py** is introduced, a sandwich supramolecular structure may be formed. Incorporation of this bipyridine into the cavity increases the rigidity of the headgroups and forces the two carboxylic groups of the ***C18*** molecule closer together. Consequently, the chiral centers of the ***C18*** molecules are packed much more closely, similar to those in linear π-conjugated systems, and this eventually causes the nanoribbon to form a twist. Up to ***C18*/4Py** = 1:2, sandwiched **4Py** continues to be incorporated and uniform twists are essentially formed, which then remain unchanged with the addition of further **4Py**.

The rigid planar structure of the bipyridine unit would seem to be an essential prerequisite for formation of the chiral twist. When **4ePy** was added, although similar structures were formed, as suggested by similar FTIR and CD spectra to those of the ***C18*/4Py** mixture, no twist was formed. This was due to the ethylene bridge between the two pyridyl rings, which imparts much flexibility to the structure.[10j] This was further demonstrated by PCMOD simulations of ***C18*/4ePy**, which showed that the distance between the intramolecular pyridyl N atoms of **4ePy** dramatically decreased from 1.00 to 0.90 nm with the introduction of one additional equivalent of **4ePy**, whereas this distance remained almost unchanged with **4Py** (Figure S8). Such structural flexibility was in complete contrast to the structural rigidity with **4Py**. This flexibility of **4ePy** meant that there was insufficient π-π stacking interaction strength to facilitate a chiral twist.

Actually, not only the rigidity of the bipyridine, but also the position of its pyridyl nitrogen atoms, as in **2Py**, had an influence on the formation of twists. FTIR data indicated that different positions of the pyridyl nitrogen atoms had a great influence on the interaction mode of the carboxylic acid–pyridyl hydrogen bonds. PCMOD results further revealed that each **2Py** could only form a hydrogen bond with one ***C18*** in forming ***C18*/2Py** assemblies, whereas **4Py** and **4ePy** could each interact with two ***C18*** in forming the respective assemblies (Figure S8). These differences ruled out the formation of a twist in the case of ***C18*/2Py** assemblies. The different modes of the carboxylic acid–pyridyl H-bonds were corroborated by CD spectroscopic analysis. ***C18*/2Py** showed a strong negative Cotton effect on account of the transcription of the chiral information from the *S*-configuration glutamic acid function (L-glutamic acid) to **2Py**. In sharp contrast, each **4Py** or **4ePy** molecule interacted with two ***C18*** amphiphiles, and the combination of the same two *S*-configuration glutamic acid functions led to a cooperative interaction of the chiral centers and induced a positive Cotton effect for the ***C18*/4Py** and ***C18*/4ePy** assemblies.[9g]

Finally, hydrophobic interactions were also essential for the formation of the twists. In the case of these homologous amphiphiles, hydrophobicity is directly related to the length of their alkyl chains. FTIR investigation revealed that the hydrophobicity of ***C16*** is analogous to that of ***C18***. Therefore, strong CD signals with the same positive Cotton effect and exclusively right-handed twists were obtained. With the shorter alkyl chains of ***C14***, imperfections in the packing of the alkyl chains were evident from FTIR measurements, which showed asymmetric and symmetric CH_2 stretching vibrations at 2921 and 2852 cm^{-1}, respectively. Consequently, in contrast to the flat ribbons of ***C18*/4Py** = 1:1 and ***C16*/4Py** = 1:1, twists started at ***C14*/4Py** = 1:1. Moreover, both right- and left-handed twists were always obtained, which was another remarkable difference from the exclusively right-handed twists of the longer-chain amphiphiles. Considering that ***C14*/4Py** = 1:2 could also form sandwich structures, we inferred that the π–π stacking and hydrophobic interactions might have competing parallel effects on the interactions of the chiral centers of ***C14***. Therefore, the kinetic balance between them invariably produced opposing right- and left-handed twists. As befits this interpretation, they were consistently CD-silent at the nanoscale. The CH_2 stretching vibrations (2922, 2852 cm^{-1}) indicated that the ***C12*** alkyl chain was more loosely packed than that of ***C18***. In addition, the carboxylic acid–pyridyl hydrogen bond di-

minished due to proton transfer from the carboxylic acid to the pyridyl N when ***C12*** interacted with **4Py**, as verified by UV/Vis spectra. As a result, the CD spectra were silent and no twist was obtained.

Conclusion

In summary, a simple supramolecular approach has been proposed to achieve chirality transcription and twisted nanostructures in a two-component system consisting of L-glutamic acid-based amphiphiles and bipyridines. The mechanism of the evolution of the chiral twist has been systematically investigated by SEM and XRD analyses, FTIR, CD, and UV/Vis spectral measurements, and molecular simulation. It is suggested that carboxylic acid–pyridine hydrogen-bonding interactions and a novel kind of sandwich-like supramolecular structure are responsible for the twist formation. The stoichiometric ratio of glutamic acid/bipyridine and the alkyl chain length also exert significant effects. In such a self-assembling system, a delicate balance between π–π stacking, hydrophobic, and chiral interactions leads to fine tuning of the nanostructures and the supramolecular chirality. Our results permit a comprehensive understanding of the self-assembly of such chiral nanostructures through the synergistic effects of multifarious noncovalent interactions. Studies on amphiphiles with unsaturated alkyl chains and/or enantiomeric glutamic head groups are underway.[18a,b]

Experimental Section

Materials: Amphiphiles ***Cn*** ($n=18$, 16, 14, 12) derived from L-glutamic acid with different alkyl tails were synthesized as reported previously[12b,17] and thoroughly characterized (see the Supporting Information). Three analytically pure bipyridines (***x*Py**), namely 4,4′-bipyridine dihydrate (**4Py**), 2,2′-bipyridine (**2Py**), and 1,2-bis(4-pyridyl)ethane (**4ePy**), were used directly as received.

Self-assembly procedures: The respective ***Cn*** (1.5×10^{-5} mol), in the form of a white solid, and deionized water (Milli-Q water, 18.2 MΩ cm, 1 mL) were mixed in a seal-capped vial, and the aqueous suspension was heated to boiling. The vial was subsequently transferred to an ultrasonic bath (100 W, 90 °C) and sonicated for several minutes until all of the solid had dissolved to give a clear solution. The hot solution was then allowed to cool naturally to ambient temperature (25 °C) at a cooling rate of about 3 °C min^{-1}, whereupon a translucent hydrogel was obtained after 30 min. For experiments involving self-assembly of the amphiphiles with the bipyridines, 0.045 M aqueous solutions of ***x*Py** were initially prepared as stock solutions. Then, the required aliquot was injected into a seal-capped vial containing the ***Cn*** (1.5×10^{-5} mol) and an appropriate amount of water was added to make a total volume of 1 mL. Thereafter, the mixtures were treated as described above. Finally, a white opaque hydrogel was obtained for ***Cn*/4Py**, while precipitates were obtained for ***Cn*/2Py** and ***Cn*/4ePy**.

Characterization: The as-prepared samples were cast on silicon wafers for scanning electron microscopy (SEM) measurements. Before SEM measurement, the sample surface was coated with a thin layer of Pt to increase the contrast. To perform transmission electron microscopy (TEM), samples were first suspended in aqueous solution and then cast on carbon-coated Cu grids. Samples in dilute aqueous suspension in quartz cells (2 mm) were used for UV/Vis and CD spectral measurements. Samples were cast on glass substrates and vacuum-dried for X-ray diffraction (XRD) measurements. Samples were first vacuum-dried and made into plates with KBr for Fourier-transform infrared (FTIR) spectral measurements.

Instruments: SEM was performed on a Hitachi S-4300 FE-SEM and TEM images were obtained on a JEM-1011 EM at accelerating voltages of 15 kV and 100 kV, respectively. FTIR spectra were recorded on a Bruker Tensor 27 FTIR spectrometer at room temperature at a resolution of 4 cm^{-1}. X-ray diffraction (XRD) analysis was performed on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with $Cu_{K\alpha}$ radiation ($\lambda=1.5406$ Å), which was operated at a voltage of 45 kV and a current of 100 mA. UV/Vis and circular dichroism (CD) spectra were obtained on JASCO UV-550 and JASCO J-815 CD spectrophotometers, respectively.

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