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PAPER

Multicomponent hydrogels from enantiomeric amino acid derivatives: helical nanofibers, handedness and self-sorting†

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In this study, chiral helical nanofibers have been obtained from suitable, co-assembling, two oppositely charged amino acid based two component hydrogels. An equimolar mixture of an *N*-terminally protected amino acid Fmoc-(L/D)Glu (Fmoc: *N*-fluorenyl-9-methoxycarbonyl, Glu: glutamic acid) and (L/D)Lys (Lys: lysine) can co-assemble to form hydrogels. These hydrogels have been characterised using circular dichroism (CD), atomic force microscopy (AFM), transmission electron microscopy (TEM), X-ray powder diffraction, fluorescence spectroscopic and rheological studies. CD and AFM studies have been extensively used to examine the chiral/achiral nature of fibers obtained from different hydrogel systems. The equimolar mixture of two L-isomers, {Fmoc-(L)Glu + (L)Lys} in the assembled state, leads to the exclusive formation of left-handed helical nanofibers, whereas an equimolar mixture of two D-isomers, {Fmoc-(D)Glu + (D)Lys}, gives rise to right-handed helical nanofibers. The CD study of the gel obtained from the {Fmoc-(L)Glu + (L)Lys} system is exactly the mirror image of the CD signal obtained from the gel of the {Fmoc-(D)Glu + (D)Lys} system. These results suggest that the molecular chirality is being translated into the supramolecular helicity and the handedness of these fibers depends on the corresponding molecular chirality in the mixture of the two component system. Reversing the handedness of helical fibers is possible by using enantiomeric building blocks. Co-assembly of racemic and equimolar mixtures of all four components, *i.e.*, [{Fmoc-(L)Glu + (L)Lys} + {Fmoc-(D)Glu + (D)Lys}] can also form hydrogels. Interestingly, in this racemic mixture self-sorting has been observed with the presence of almost equal amount of left- and right-handed helical nanofibers. The equimolar mixture of Fmoc-(L)Glu and L-ornithine/L-arginine also produces hydrogel with left-handed helical fibers. Moreover, the straight fiber has been observed from the two component hydrogel {Fmoc-(L)Glu + (L)Lys} system in the presence of Ca^{2+}/Mg^{2+} ions. This indicates the straight nanofibers are obtained under suitable conditions and acid–base interaction is responsible for making the helical fibers at the nanoscale.

Introduction

Helicity is omnipresent in nature ranging from nanoscopic helical structures in proteins, DNA double helices and collagen triple helix structures to microscopic viruses and macroscopic seashells. Chirality plays a pivotal role in chemistry, biology and material sciences through its various applications in chemical-/bio-sensors, pharmaceutics, chiral catalysts, asymmetric synthesis, enantioselective separation, nonlinear optics, chiral devices, and also in other fields.[1] Being inspired by the importance of chirality in biology and to explore interesting applications of chirality in nanosciences, chemists have attempted to make helical structures using molecular assembly of one or multicomponent(s).[2] Chirality can be expressed at different levels, from chiral small molecules to helical conformation of macromolecules, and even to helical supramolecular nanostructures. Molecular assembly based on the rational control of noncovalent interactions including hydrogen bonding, aromatic

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† Electronic supplementary information (ESI) available: Fig. S1–S14; FT-IR spectrum of a dried hydrogel, CD spectra of two component systems in the solution state, CD spectra of two component hydrogels obtained from {Fmoc-(L)Glu + (L)ornithine} and {Fmoc-(L)Glu + (L) arginine} separately, CD spectrum of {Fmoc-(L)Glu + (L)Lys} in DMSO/water mixture, size distribution of width of fibers obtained from {Fmoc-(L)Glu + (L)Lys}, AFM images of two component hydrogels [Fmoc-(L)Glu + (L)arginine] and [Fmoc-(L)Glu + (L) ornithine], TEM image of hydrogel {Fmoc-(L)Glu + (L)Lys}, size distribution of widths of these fibers obtained from {Fmoc-(D)Glu + (D)Lys}, AFM image of two component hydrogel {Fmoc(L)Glu + (L) Lys} in the presence of 0.5 equimolar Ca^{2+}, AFM image of two component hydrogel {Fmoc(L)Glu + (L)Lys} in the presence of monovalent Na^+ and K^+, HRMS and ^{1}H NMR spectra of synthetic Fmoc-(L)Glu and Fmoc-(D)Glu, titration curve for pK_a determination. See DOI: 10.1039/c1sm05907f

stacking, electrostatic interactions, van der Waals interactions and/or metal coordination interactions provides powerful tools for the design and construction of hierarchical structures from nano- to micrometre scale.[2,3]

There are several reports of constructing supramolecular helical nanostructures including helical fibers,[4] helical ribbons,[1h,2g,5] or helical tubes[6] by using different strategies from self-assembling organic molecules. Meijer and his workers have produced supramolecular helical polymers using the self-recognition of hydrogen bonds.[2h] A long fiber with left handed helicity has been obtained from a disk-shaped molecule with chiral tails upon self-assembly in chloroform and also a nonhelical rod has been formed in the presence of potassium ions.[4a] The formation of left-handed helical nanoropes has been reported from the self-assembly of a rigid π-conjugated oligo(*p*-phenylenevinylene) with remote chiral handles.[4b] Yashima and his coworkers have reported supramolecular cholesteric twist based on controlled polymerization of an enantiomerically pure isocyanide.[4d] Stupp and his coworkers have developed a class of tripeptide amphiphiles that are self-assembled to form superhelical twisting nanofibers.[4f] Liu and coworkers have made helical nanofibers based on gels containing achiral porphyrin units.[4g] Huang and coworkers have reported the double stranded helical nanofibers based on a sugar–lipid amphiphilic hydrogel.[4i] Hamley and coworkers have reported the formation of a helical nanoribbon based on a short segment of amyloid β peptide.[5d]

Helical to nonhelical conversion and even inversion of helicity in supramolecular assembly and also in certain macromolecules can be achieved by using either enantiomeric molecular building blocks,[7] or by the slight structural change in the molecular building blocks,[8] or by the changing solvent or temperature,[6d,9] or upon binding with chiral/achiral counterions,[10] or upon binding with chiral/achiral neutral guest molecules,[11] or by changing the pH,[12] or by irradiating with light.[4e,13] The inversion of the handedness of a helical fiber using the enantiomeric form of the molecular building block is an interesting phenomenon.[7] One of the oldest reports in the construction of helical nanofibers was based on a supramolecular liquid-crystalline polymer consisting of the polyassociation of the complementary chiral components TP2 and TU2, which were derived from the nucleobase pyrimidine (P) and uracil (U) derivatives and from the D, L, or *meso* forms of tartaric acid (T).[7a] The handedness of helical fibers is governed by the chirality of the tartaric acid. Other examples of the formation of helical fibers include the self-assembly of dithienylethene functionalized chiral amides,[7c] dendron rodcoil triblock molecules[7d] and artificial β-sheet-conforming peptides.[7e] The handedness of the helical fibers can be reversed by using the mirror-image form of the molecular building block. Previous results of our research group have shown that the handedness of the helical nanofibers can be reversed either by using mirror-imaged tri-amide molecules[7f] or by utilizing the enantiomeric form of pseudopeptide-based building blocks.[7h]

The principle of self-sorting is efficiently used in nature in the formation of functional architectures like DNA. In DNA four nucleobases (adenine (A), thymine (T), guanine (G), and cytosine (C)) self-sort to form specific self-complementary base pairs (AT and GC) in DNA hybridisation. This self-sorting principle is also found in the crystallization of racemates into conglomerates. Lehn and his coworkers have shown that the racemic mixture of helical fiber forming components gives rise to spontaneous resolution to form both left- and right-handed supramolecular helical nanofibers in the liquid-crystalline system in chloroform.[7a] This type of self-sorting phenomenon has been observed in other artificial systems.[14] Examples include the occurrence of self-sorting in a multi-component mixture of functionalized different organic groups (crown ethers and ammonium ions),[14a] and tetra-urea calix[4]arenes system.[14b] A self-sorting phenomenon is also observable in some organogel systems including dendritic peptide,[14d] perylene bisimide derivative[14e] and long chain containing carbamate based chiral pyrrolidine derivatives.[14g] In dendritic peptide based assembly, Smith and coworkers have investigated three parameters namely "size", "shape" and "chirality".[14d] They have observed that the mixtures of dendritic peptides with different "size" and "chirality" can be self-organized in their molecular scaffolds, whereas mixtures of dendritic peptides with different "shapes" can break one another's self-association process.[14d] Chiral pyrrolidine derivative based organogels obtained from the two enantiomers of gelators and their mixtures exhibited enantiomeric discrimination and this results in a self-sorting process.[14g]

However, none of these above mentioned examples address multiple issues including reversing the handedness of helical fibers, disrupting the helicity and the self-sorting of both left- and right-handed helical fibers in two or multicomponent systems. In this study, we present the construction of chiral helical nanofibers from the co-assembly of the complementary amino acid based two component hydrogel system, reversing the chirality of helical fibers by changing the intrinsic molecular chirality of constituent amino acid building blocks, self-sorting of both left- and right-handed helical nanofibers in a four component racemic mixture and disrupting the helicity of nanofibers in the presence of Ca^{2+}/Mg^{2+} ions. The equimolar mixture of two L isomers, {Fmoc-(L)Glu + (L)Lys}, forms left-handed helical nanofibers, whereas an equimolar mixture of two D isomers, {Fmoc-(D)Glu and (D)Lys}, results in right-handed helical nanofibers. Moreover, the racemic mixture of the above mentioned four component system, *i.e.*, [{Fmoc-(L)Glu + (L)Lys} + {Fmoc-(D)Glu + (D) Lys}], yields the co-existence of helical nanofibers of opposite handedness, indicating the occurrence of the self-sorting process. Interestingly, an achiral straight fiber has been obtained from the multicomponent hydrogel system involving {Fmoc-(L)Glu and (L)Lys} in the presence of Ca^{2+}/Mg^{2+} ions. This suggests that the presence of acid–base interactions involving two oppositely charged amino acids in a co-assembling system can play a role in the formation of chiral (helical) fibers. To the best of our knowledge, this is the unique example of the observation of several phenomena including construction of helicity, reversing of helicity, self-sorting of both left- and right-handed helical fibers and abolishing the helicity of the fibers based on co-assembly of the multicomponent hydrogel system under specific conditions.

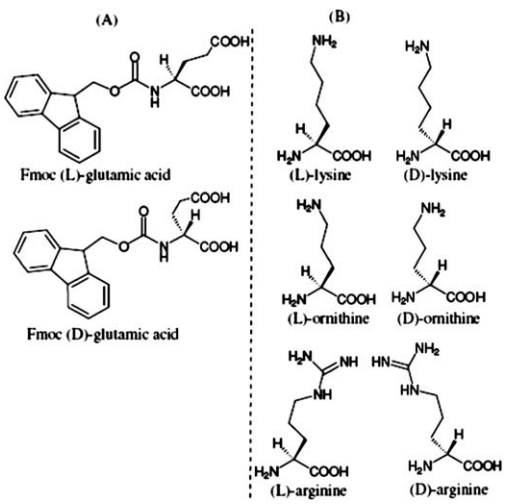
Results and discussion

Gel formation and characterization

Low molecular weight supramolecular hydrogels are an interesting class of soft materials.[15] Formation of two-component gels

through supramolecular complex formation is an emerging field of research.[16] Recently, Fmoc containing small molecule based hydrogels have been reported.[17] In this study, assembling properties of the two component system, Fmoc-Glu and Lys (see Scheme 1), were first examined by gelation experiments in water at pH 7.4 using phosphate buffer as well as distilled water (milli Q). Several attempts using different approaches were made to examine whether Fmoc-(L/D)Glu alone can form hydrogels or not. Fmoc-(L/D)Glu exhibited very low solubility in distilled water (milli Q) at pH 7.4 even at high temperature (~100 °C). However, by cooling down the temperature to room temperature, the soluble portion was precipitated out. The Fmoc-(L/D)Glu showed moderate solubility at pH 7.4 using phosphate buffer at high temperature and precipitation was observed upon cooling down the temperature to room temperature. The Fmoc-(L/D)Glu alone is also unable to form any kind of hydrogel using the phosphate buffer under the condition studied (pH 1–11). The Fmoc-(L/D)Glu did not show any hydrogel formation using sodium carbonate or sodium hydrogen carbonate or sodium hydroxide. No hydrogel from Fmoc-(L/D)Glu was found, by dissolving it in basic pH and then decrease the pH of the medium gradually using AcOH or using the hydrolysis of glucono-δ-lactone (GdL) as described elsewhere.[17d]

The equimolar mixture of these two components {Fmoc-(L)Glu + (L)Lys} was dissolved in water by heating for a few minutes. A translucent hydrogel was obtained, when this hot solution was cooled down to room temperature (Fig. 1, inset). The minimum gelation concentration is 0.05 (M) with respect to each of these components using phosphate buffer solution at pH 7.4 and the hydrogel is stable within the pH range 2–9 using phosphate buffer. The final pH values after mixing both components in all cases were changed. After hydrogel formation the pH was determined using the pH meter. After gel formation using buffer solution at pH 7.4 and 9.0, the pH of the hydrogels were decreased to pH 5.20 and 5.38 respectively. However, the increase in pH from 2.0 to 4.16 was observed, when the two component gel was formed using the buffer solution at pH 2.0. A



Scheme 1 Chemical structures of the components involved in two component hydrogels: (A) acidic side chain containing amino acid and (B) basic side chain containing amino acids.

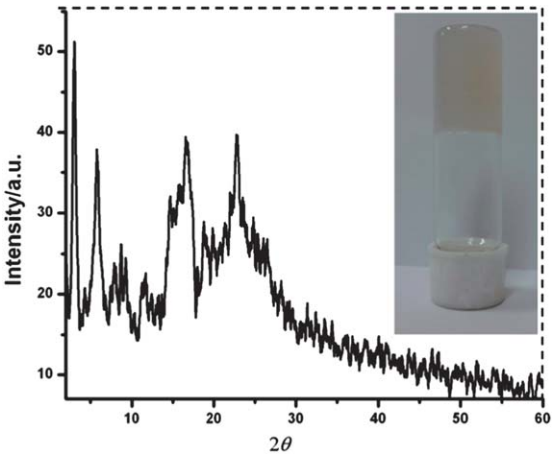
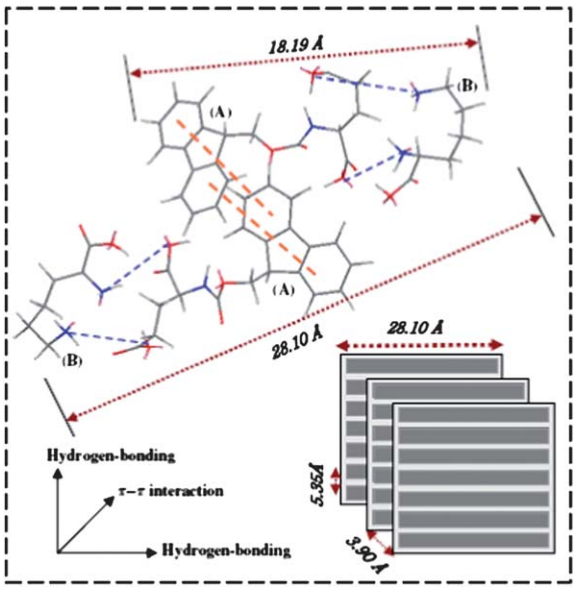


Fig. 1 X-ray powder diffraction of dried hydrogel obtained from the two component system [Fmoc-(L)Glu + (L)Lys]. A photograph of hydrogel obtained from [Fmoc-(L)Glu + (L)Lys].

viscous solution was observed from the two component system above pH 9 and upto pH 10 using phosphate buffer. However, a clear solution was obtained with a further increase in the pH above 10 using the buffer. No gel formation was observed using buffer solution below pH 2.0, instead a precipitation was occurred. On the basis of pK_a values obtained from the titration experiment, the degree of ionizations of two COOH groups present in Fmoc-Glu and one COOH group and two NH_2 groups in lysine have been calculated at the final pH value of 5.2 within the hydrogel. In this case the degree of ionizations (or deprotonation) of α-COOH and side chain-(γ)-COOH, of Fmoc-Glu, were found to be 0.9754 and 0.585 respectively. The degree of ionization of α-COOH and the degree of protonation of α-NH_2 and side chain-(ε)-NH_2 of lysine were determined to be 0.99991, 0.99968 and 0.999995 respectively. The degree of ionization of COOH groups and the degree of protonation of NH_2 groups of the two component system in other pH values are mentioned in the ESI†.

This gel is thermoreversible in nature and the T_{gel} is found to be 41 °C. By mixing these two oppositely charged amino acids (Fmoc-(L)Glu and (L)Lys) in water a supramolecular hydrogel is formed *via* the electrostatic attraction (acid–base type) triggered co-assembly (see Scheme 2). The FT-IR study indicates the presence of intermolecular hydrogen bonding interaction between the amino acid backbones and the X-ray powder diffraction study suggests the existence of π–π stacking interaction between the aromatic fluorenyl rings, in the gel state (Fig. S1† in the ESI and 'X-Ray powder diffraction study' section discussed later). So electrostatic interaction, hydrogen bonding and π–π stacking interactions are the driving force for hydrogelation. It is important to note that the lysine can be replaced only either by ornithine or by arginine among all other amino acids to produce hydrogels. This suggests that simple acid–base interaction can be responsible for the co-assembly and hydrogelation as at pH 7.4, two carboxylic groups of Glu are deprotonated and two amino groups of lysine/ornithine and one amino and one guanidino group of arginine are protonated. Other proteinaceous amino acids (Glycine, Alanine, Valine, Leucine, Isoleucine, Phenylalanine, Tyrosine, Tryptophan,



Scheme 2 Tentative model for the molecular packing of gelator molecules in the assembled state. Blue dotted lines indicate acid–base type interactions, while orange dashed lines indicate aromatic π–π stacking interactions. Molecules A {Fmoc-(L)Glu} and B {(L)Lys} are involved in acid–base interactions to form a co-assembled adduct first, and this is further assembled to form a bilayer structure. This bilayer structure acts as a repeating structural unit and each black block line indicates one of these structural units.

Histidine, Proline, Aspartic acid, Glutamic acid) with only one primary amino group are unable to co-assemble with Fmoc-Glu to form hydrogel. The mixture of Fmoc-Glu and any other amino acids (other than lysine, arginine and ornithine) remains insoluble in distilled water. This suggests that for co-assembly and/or hydrogelation acid–base type interactions between two carboxylic acid groups of Fmoc-Glu and two amino/guanidino group(s) of lysine/ornithine/arginine are responsible. These co-assembling adducts can be further assembled using π–π stacking interactions utilizing aromatic moieties (of Fmoc-Glu residue) and hydrogen bonding to form gel phase materials (see Scheme 2). Gelation tests were also performed using propyl amine (one and two equivalent separately) and one equivalent of organic diamines (1,3-diamine or 1,4-diamine or 1,6-diamine) with Fmoc-(L/D)Glu. However, no gelation was observed in any of these cases. This suggests that two amino groups containing amino acids were required for this type of multicomponent based hydrogelation.

X-Ray powder diffraction study

X-Ray powder diffraction, a technique for ascertaining the molecular packing of assemblies, was used to get the internal assembling structure of the co-assembling two component hydrogel. Fig. 1 shows the small angle X-ray powder diffraction (XRPD) patterns of the xerogel obtained from the {Fmoc-(L)Glu + (L)Lys} system. A strong reflection peak corresponding to a *d*-spacing of 15.29 Å (at $2\theta = 5.77$) was found and this *d*-spacing value is nearly close to the calculated molecular length (18.19 Å) of the co-assembled state. In the small angle region (at $2\theta = 3.03$) one sharp peak corresponding to a *d*-spacing of 29.07 Å was observed, which may correspond to the higher order lamellar organization of the co-assembling molecules. In the higher angle region, a peak around $2\theta = 22.76$ ($d = 3.90$ Å) is a characteristic of the π–π stacking distance of two aromatic fluorenyl groups.[18] Another peak at $2\theta = 16.55$ ($d = 5.35$ Å) corresponds to the distance between the two hydrogen bonded molecules in a strand.[18] Fmoc-(L)Glu and (L)Lys are involved in acid–base interactions to form a coassembled adduct (a pair) and these co-assembled adducts are further assembled to form a bilayer structure by π–π stacking interactions in the assembled gel state. The length of 2.907 nm (obtained from XRPD) is larger than the extended coassembled adduct's length (1.819 nm). However, it is smaller than two times the co-assembled adduct's length. To satisfy the intermolecular hydrogen bonding interaction, acid–base interaction and π–π stacking interaction, we believe that assembled adducts form bilayer structures (having a width of 2.81 nm) and this bilayer structure is the repeating structural unit.[13d] The width of a bilayer structure (2.81 nm) is calculated from the energy minimized tentative model structure and it is comparable with the distance obtained from the small angle XRPD diffraction peak (2.907 nm). Based on these above observations a tentative model of molecular packing has been proposed in Scheme 2.

Circular dichroism study

Circular dichroism (CD) is a useful tool for determining the chiral molecular arrangement in assemblies. This is because intermolecular interactions, especially between chromophoric molecules, may produce striking chiroptical responses and generate CD signals often much stronger in associated state compared to their isolated molecular state. The CD study of two component hydrogels at the gel state with different stereochemical compositions is presented in Fig. 2. Circular dichroism of the gel obtained from {Fmoc-(L)Glu + (L)Lys} has shown a strong negative signal around 304 nm. The Cotton effect at 304 nm (π–π* transition) indicates the superhelical arrangement formed by the fluorenyl groups in the hydrogel state[16d] and the CD signal at 304 nm is presumably induced by the formation of chiral

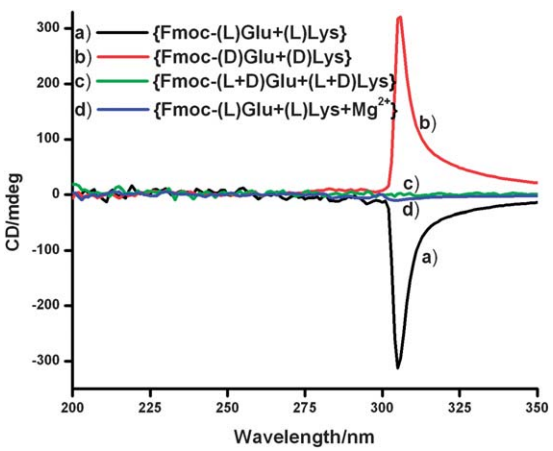


Fig. 2 CD spectra of hydrogels at the near gel state with different stereochemical compositions as indicated in the figure.

(helical) structures. It can be noted that the amide region in the CD spectra (200–230 nm) is noisy due to the high absorbance in this region, with the high concentration of gelators.[17e] However, in the solution state with low concentration of gelators, a Cotton effect at 223 nm containing positive signal appeared (Fig. S2, ESI†). This is due to n–π* transition.[16d]

Moreover, it can be mentioned that each of these hydrogels obtained from {Fmoc-(L)Glu + (L)ornithine} and {Fmoc-(L)Glu + (L)arginine} also produces a strong negative signal around 306 nm (Fig. S3, ESI†). The CD spectrum of {Fmoc-(D)Glu + (D)Lys} in the gel state has shown a strong positive signal around 304 nm and this CD signal is nearly the mirror image of the CD signal obtained from the {Fmoc-(L)Glu + (L)Lys} gel system (see Fig. 2). This suggests that the chirality of the gel obtained from the co-assembly of {Fmoc-(L)Glu + (L)Lys} is opposite in nature with respect to the gel obtained from the D-isomers, *i.e.*, {Fmoc-(D)Glu + (D)Lys}.

This type of chirality is generated due to the formation of supramolecular chirality in the gel state.[5c] To establish this temperature dependent, concentration dependent and solvent dependent CD studies have been performed. In the case of the temperature dependent CD study (see Fig. 3), the signal at 304 nm has been gradually decreased with an increase in the temperature and surprisingly the signal has approached almost the base line at the temperature higher than the T_{gel} value, where gelator molecules remain in the solution state and not in the assembled state. This clearly suggests the presence of supramolecular chirality in the co-assembled state. The temperature dependency of the CD signals clearly suggests that the CD response is a consequence of the co-assembly of chiral components to supramolecular chirality, rather than the inherent molecular chirality of the individual amino acid components.[5c,16j] Thus, each of these two component systems (*e.g.*, {Fmoc-(L)Glu + (L)Lys}) has appeared as a supramolecular chiroptical switch in the sol–gel process. However, the chirality disappeared when the gel was heated to solution, and it reappeared again upon cooling the system to get the gel phase material. In DMSO/water or 1,4-dioxane/water solvent mixture, the mixture of these two components remains in the solution state at the similar concentration that is required for gelation in water. There is no characteristic CD of signal of {Fmoc-(L)Glu + (L)Lys} in DMSO/water or 1,4-dioxane/water solvent mixture (see Fig. S4, ESI†). This further supports the fact that the CD signal of the hydrogel is arising from the supramolecular chirality generated in the co-assembled gel state and it does not arise from the individual chirality of the corresponding amino acid components.

Interestingly, the CD spectrum of the gel obtained from the racemic mixture of both L and D isomers of these components, *i.e.*, [{Fmoc-(L)Glu + (L)Lys} + {Fmoc-(D)Glu + (D)Lys}] is almost flat and it is close to the baseline (see Fig. 2). The observed almost zero Cotton effect for [{Fmoc-(L)Glu + (L)Lys} + {Fmoc-(D)Glu + (D)Lys}] suggests that the inter-chromophore orientation is either disordered, achiral, or is chiral but racemic (*i.e.* equal amounts of left- and right-handed helical orientations are present).[2a] Similarly, in the presence of divalent cations Ca^{2+} or Mg^{2+} this two component system (*e.g.*, {Fmoc-(L)Glu + (L)Lys}) does not show any characteristic CD signal (see Fig. 2) suggesting the achiral nature of the supramolecular aggregates in the presence of any of these divalent metal ions (Ca^{2+} or Mg^{2+}). The molar ratio of divalent cations (Ca^{2+} or Mg^{2+}) to gelators is 1 : 1.

Morphological study

To investigate the morphology of the binary component hydrogels microscopic experiments were carried out using atomic force microscopy (AFM). Fig. 4–6 show the tapping mode AFM images of hydrogels with two different stereochemical compositions {Fmoc-(L)Glu + (L)Lys} and {Fmoc-(D)Glu + (D)Lys} and their racemic mixture.

An AFM image of the hydrogel obtained from {Fmoc-(L)Glu + (L)Lys} is shown in Fig. 4 and this clearly indicates the exclusive presence of the network structure of one dimensional helical nanofibers with a few micrometres in length. Fig. 4 denotes that the widths of these helical fibers are within the

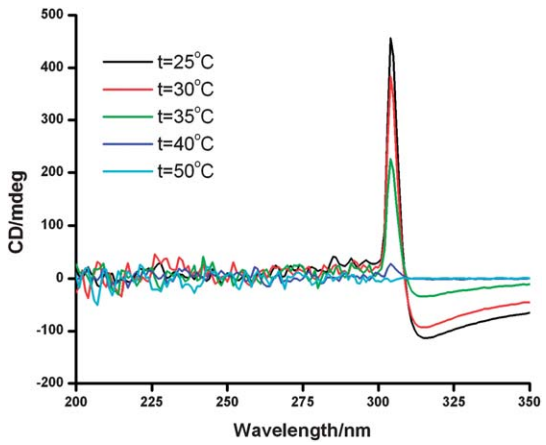


Fig. 3 Temperature dependent CD spectra of {Fmoc-(D)Glu + (D)Lys} hydrogel at the respective gel state starting from 25 °C (room temperature) to 50 °C (>T_{gel}).

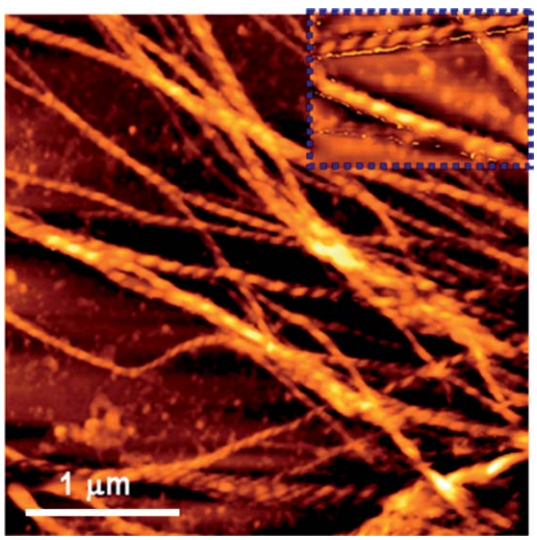


Fig. 4 AFM image of two component hydrogel [Fmoc-(L)Glu + (L)Lys] showing clearly the presence of left handed helical fibers; inset shows the helicity of single fibers.

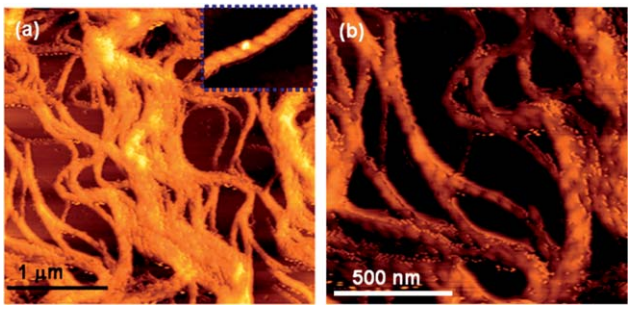


Fig. 5 (a) AFM image of two component hydrogel [Fmoc-(D)Glu + (D) Lys] showing right handed helical fibers; inset shows the helicity of single fiber; (b) zoomed version of some part of the image (a).

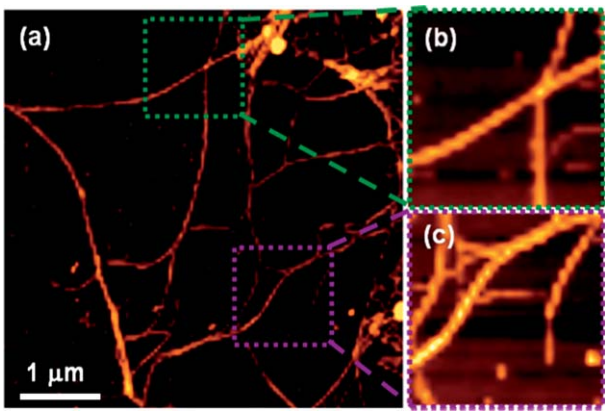


Fig. 6 (a) AFM image of racemic mixture in multi-component (four componets) hydrogel [Fmoc-(L + D)Glu + (L + D)Lys] showing the presence of both left- and right-handed helical fibers; (b) zoomed version of green color marked region showing the right-handed helical fiber clearly; (c) zoomed version of violet color marked region showing the left-handed helical fiber clearly.

range 52–127 nm and the majority of these fibers fall within the range 60–100 nm (Fig. S5, ESI†) with an average diameter of 82.52 nm. The morphology of a single helix is twisted with uniform left-handed bias along the fiber long axis (see Fig. 4). The helical pitch of these fibers varies from 98 to 140 nm from one fiber to the other fibers. However, the helical pitch of a single helical fiber remains uniform along the fiber and this indicates that the underlying forces causing helix formation are uniform throughout the fiber structure. The observed left-handed helicity is compatible with the observed negative Cotton effect for the circular dichroism (CD) measurements.[19] It can be mentioned that hydrogels obtained from {Fmoc-(L)Glu + (L)ornithine} and {Fmoc-(L)Glu + (L)arginine} also individually produce left-handed helical nanofibers (see Fig. S6, ESI†). This suggests that simple acid–base interactions are responsible for the co-assembly in the formation of hydrogel and helical fibers.

A TEM experiment was also carried out using the two component hydrogel {Fmoc-(L)Glu + (L)Lys} system to examine the morphological inner detail of helical structure and to probe whether it is a fiber or a tube (with inner hollowness). The TEM image is shown in Fig. S7† in the ESI section and this image clearly demonstrates the formation of helical nanofibers, instead of a helical nanotubular structure.

On the other hand, AFM image analysis of the hydrogel formed by {Fmoc-(D)Glu + (D)Lys} reveals the presence of the network structure of right handed helical nanofibers (see Fig. 5). These helical fibers are a few micrometres in length and the width of these fibers varies from 62 to 135 nm, with an average diameter of 84.5 nm. The majority of these fibers fall within the range of 62–99 nm (Fig. S8, ESI†). The pitch length of the helical fibers varies from 70.5 to 90 nm. However, the pitch of a single fiber is uniform in nature. Therefore, it can be concluded that the helicity of fibers could be easily controlled by the chirality of the constituent amino acid components of the hydrogel system.

It is interesting to examine the morphology of the gel obtained from the racemic mixtures {Fmoc-(L + D)Glu + (L + D)Lys} of the four component system. There are three following possibilities: (a) change in the morphology of helical to non-helical (straight) fibers or any other shape, (b) co-existence of both left- and right-handed helical fibers within the same system and (c) the presence of both left- and right-handedness within the same helical fiber with one half left handed and other portion right handed.

However, the AFM images of hydrogels obtained from racemic mixture {Fmoc-(L + D)Glu + (L + D)Lys} reveal the presence of both left- and right-handed helical fibers in the same system and not within the same fiber (see Fig. 6). In this study, widths of both left- and right-handed fibers are within the range of 70–90 nm. This spontaneous occurrence of racemate resolution by chiral selection in molecular recognition directed co-assembly of the components in the supramolecular hydrogel system is rare.[7a] In most of these cases a racemic mixture produces either achiral morphology *e.g.* straight fiber or a different morphology like vesicles.[7e] However, in this study, self-sorting behavior of these components has been observed. The chirality at the supramolecular level depends on the configuration of the stereogenic centers of the amino acids in the two component hydrogel system.

It is interesting to address the point whether in the presence of divalent cations Ca^{2+} or Mg^{2+} the hydrogel based helical fibers are formed or not. Straight fibers are obtained from this two component hydrogel system in the presence of divalent cations Ca^{2+}/Mg^{2+} with 1 : 1 molecular ratio (see Fig. 7). Fig. 7 shows that no helical (left- or right-handed) fibers have been formed and only straight fibers have been observed with an average width of 170 nm. Therefore, helical fiber to straight fiber

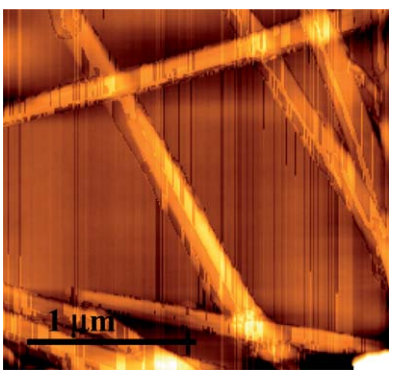


Fig. 7 AFM image of aggregates obtained from {Fmoc-(L)Glu + (L) Lys} in the presence of Ca^{2+} ions.

transformation is possible in the presence of bivalent metal ions such as Ca^{2+} or Mg^{2+}. This is because Ca^{2+} ions can easily bind to the two carboxylate moiety of Fmoc-glutamic acid. This inhibits the co-assembly process between Fmoc-glutamic acid and lysine/ornithine/arginine using acid–base type interaction, which is responsible for helicity. In this study, the gel formation is not affected by the presence of Ca^{2+}/Mg^{2+} ions, however the morphology of the hydrogel changes from helical to straight fibers upon binding with Ca^{2+} or Mg^{2+} into the multicomponent gel system.

AFM experiments have also been carried out using different concentrations of divalent cations (Ca^{2+}/Mg^{2+}) to explore the dependency of helical to non-helical transformation of gel nanofibers on the concentration of divalent cations. At lower concentration of Ca^{2+} ions, both helical and non-helical (straight) gel fibers have been observed (Fig. S9, ESI†). However, at the relatively higher concentration of Ca^{2+} ions, *i.e.*, the equimolar ratio of each of the gelators and Ca^{2+} ions, only straight nanofibers have been obtained. In other words, it can be stated that to disrupt the helicity completely the required molar ratio of divalent metal ions to gelators is 1 : 1. It is interesting to observe that in the presence of monovalent metal ions (*e.g.*, Na^+, K^+) two component hydrogel systems also produce helical nanofibers (Fig. S10, ESI†). This suggests that helical to non-helical transition is due to the binding of divalent metal ions with two carboxylic acid of glutamic acid residue.

Fluorescence study

Fluorescence experiments have been utilized to follow the assembling nature of these gelator molecules within hydrogels because the fluorescence study may provide useful information regarding the change in the microenvironment of the fluorophore moiety during the gelation process. The concentration dependent fluorescence starting from very dilute solution to the assembling gel state has been studied and it has been shown in Fig. 8, where (a) is a very dilute solution of gelators at a concentration of 0.0031 (M), (b) is a dilute solution of gelators at a concentration of 0.0062 (M), (c) is a solution of gelators at a concentration of 0.0125 (M), (d) is a concentrated, viscous solution of gelators at a concentration of 0.025 (M) and (e) is the gel state of gelators at a concentration of 0.0500 (M) (minimum gelation concentration). Following observations have been noted.

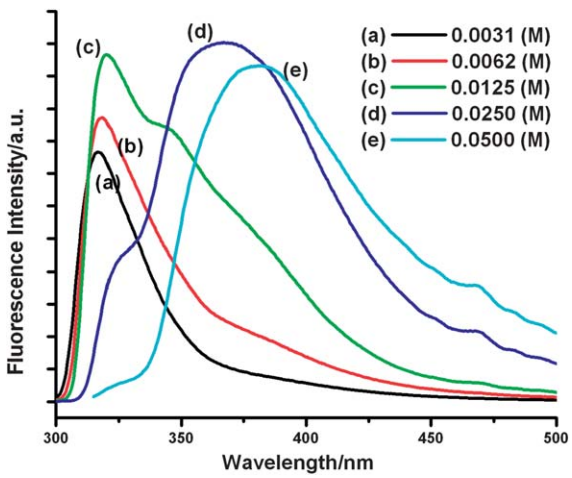


Fig. 8 Concentration dependent fluorescence spectra of two-component gelators {Fmoc-(L)Glu + (L)Lys} in water starting from very dilute solution (concentration 0.0031 M) to gel state (concentration 0.05 M) as indicated in the figure.

(1) In the case of (a), the strong emission maximum centered at 317 nm has been obtained for the excitation at 300 nm. This emission is arising from monomeric Fmoc-Glu molecules.[16d,i,20] Fluorescence intensity slowly increases by increasing the concentration from (a) to (c). This is due to the enhancement of concentrations of gelator molecules. (2) By increasing the concentrations of both gelators further, *i.e.* the enhancement of concentration (c) sol to (d) viscous solution, a huge red shifting of fluorescence emission maximum has been observed from 320 nm to 367 nm, without changing the emission intensity significantly. This indicates the presence of aggregation at this state. (3) Further enhancement of both gelator's concentration from (d) to gel state (e) has resulted in a red shifting from 367 nm to 380 nm. The emission maximum at 380 nm suggests that fluorenyl groups are dimerized in the gel state due to a strong π–π interaction[16d,i] (Scheme 2). In last two cases, *i.e.* in the concentration region of (d) and (e), a small shoulder emission peak at 468 nm has also been observed. This indicates that some fluorene moieties aggregate more efficiently involving more than two fluorene groups in π–π stacking interactions in the hydrogel state.[16d,i]

Rheological study

Viscoelastic properties of two component hydrogels at different stereo-chemical compositions were examined by measuring their rheological properties using these gels at a fixed concentration 0.2 (M) with respect to each of these components. In a typical frequency sweep experiment, the variation of storage modulus (G') and loss modulus (G'') was monitored as a function of applied angular frequency under a constant strain 0.1%. It is worth mentioning that G' and G'' respectively symbolize the ability of the deformed material to restore its original geometry and tendency of a material to flow. For an ideal liquid, $G' = 0$, and for an ideal solid, $G'' = 0$. For viscoelastic materials like gels, G' is greater than G'', and it shows that elastic behavior of the system is dominant. Fig. 9 shows the linear viscoelastic frequency sweep responses of these hydrogels. All of these

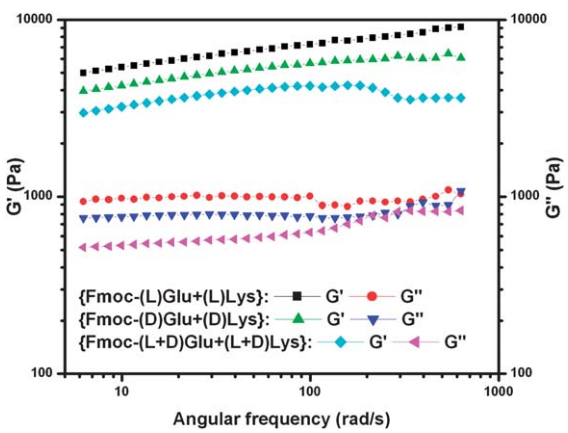


Fig. 9 Frequency dependence of the dynamic storage moduli (G') and the loss moduli (G'') of hydrogels at different stereo-chemical compositions as indicated in the figure.

multi-component systems at different stereo-chemical compositions exhibit a very weak frequency dependence within the experimental frequency limit, with G' greater than G''. This suggests that they are effective physical hydrogels.

Conclusions

This study addresses multipurpose issues: formation of helical (chiral) nanofibers, reversing the handedness of helicity and self-sorting of both left- and right-handed helical nanofibers. In this study, one-dimensional helical nanofibers are successfully constructed from suitable co-assembling complementary chiral amino acid based two component hydrogel systems utilizing acid–base type interaction (electrostatic interaction), hydrogen-bonding and aromatic π–π stacking interactions. This study also demonstrates the reversing of handedness of the helical (chiral) nanofiber using the enantiomeric form of constituent amino acids, the conversion of helical to straight fibers in the presence of bivalent metal ions such as Ca^{2+}/Mg^{2+} and self-sorting of both left- and right-handed helical fibers in a racemic mixture of all four L and D components of the amino acid based gel system. These observations suggest that the molecular chirality is being transferred into the supramolecular chirality and ultimately to the nanoscale level (helical nanofiber) and the handedness of these helical nanofibers can be reversed by using the enantiomeric molecular building blocks. These findings also indicate that the presence of acid–base interactions between two oppositely charged amino acids can have a definite role in the helical fiber formation as the presence of Ca^{2+}/Mg^{2+} ions disrupts the co-assembly of Fmoc-(L/D)Glu and (L/D)Lys.

Experimental section

Materials

L-Glutamic acid, D-glutamic acid, L-lysine, D-lysine, L-arginine, L-ornithine and Fmoc-chloride were purchased from Sigma-Aldrich. The water used in all experiments was of Millipore Milli-Q grade.

Synthesis of Fmoc-Glu

2 mmol of Glu was dissolved in a basic sodium carbonate solution (15 mL). It was cooled in an ice-water bath and a cooled solution of 3 mmol Fmoc-Cl in dioxane (15 mL) was added to it. The reaction mixture was allowed to come to room temperature and stirred for 24 h. Then the solution was concentrated in vacuum to about 15 mL, cooled in an ice water bath, covered with a layer of ethyl acetate (about 30 mL), and acidified with a dilute HCl to neutral pH. The aqueous phase was extracted with ethyl acetate and this operation was done twice. The ethyl acetate extract was pooled, dried over anhydrous Na_2SO_4 and evaporated in vacuum. A white material was obtained and this was characterized by mass spectrometry, ^{1}H-NMR spectroscopy (for spectra see Fig. S11–S13†).

Circular dichroic (CD) study

Circular dichroism spectroscopy was used for determining the chiral molecular arrangement of assemblies within hydrogels. All CD spectra were recorded by using a quartz cuvette of 1 mm path length in a Jasco J-815 spectropolarimeter. All the CD experiments were performed for gel samples (homochiral and racemic) using the same gelators concentration.

Atomic force microscopic (AFM) study

Morphologies of these reported hydrogels were investigated using a tapping-mode atomic force microscope (AFM). AFM studies were done by placing a small amount of wet hydrogel at its minimum gelation concentration on a microscope cover glass. The material was then allowed to dry in air by slow evaporation first and then under vacuum at room temperature for two days. Images were recorded by exploiting an Autoprobe CP Base Unit di CP-II instrument (model no. AP-0100).

X-Ray powder diffraction (XRPD)

XRPD of dried hydrogel material was performed by using an X-ray diffractometer (Bruker D8 Advance) equipped with a conventional CuK_α X-ray radiation ($\lambda = 1.54$ Å) source and Bragg diffraction setup (Seifert 3000P).

Transmission electron microscopic (TEM) study

The morphology of the two component hydrogel obtained from {Fmoc-(L)Glu + (L)Lys} was investigated using a transmission electron microscope (TEM). The sample was prepared through depositing a small amount of the near gel phase material on a TEM grid (300 mesh Cu grid) coated with Formvar and carbon film. The grid was then allowed to dry under vacuum for two days. A TEM image was taken by a JEOL electron microscope operated at an accelerating voltage of 200 kV.

Fluorescence spectroscopy

The emission spectra were recorded by using a Horiba Jobin Yvon Fluoromax 3 instrument with a 1 cm path length quartz cell in a concentration range from 0.0031%, w/v, to 0.050%, w/v (MGC). The excitation and emission slit width were 5 and 5 nm, respectively.

Rheological study

A rheological experiment was performed with an AR 2000 advanced rheometer.

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