Chirality

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Macroscopic Chirality of Supramolecular Gels Formed from Achiral Tris(ethyl cinnamate) Benzene-1,3,5-tricarboxamides**

Zhaocun Shen, Tianyu Wang, and Minghua Liu**

Abstract: *A C_3-symmetric benzene-1,3,5-tricarboxamide substituted with ethyl cinnamate was found to self-assemble into supramolecular gels with macroscopic chirality in a DMF/H_2O mixture. The achiral compound simultaneously formed left- and right-handed twists in an unequal number, thus resulting in the macroscopic chirality of the gels without any chiral additives. Furthermore, ester–amide exchange reactions with chiral amines enabled the control of both the handedness of the twists and the macroscopic chirality of the gels, depending on the structures of the chiral amines. These results provide new prospects for understanding and regulating symmetry breaking in assemblies of supramolecular gels formed from achiral molecular building blocks.*

Supramolecular gels have been carefully investigated as a soft matter with lots of potential applications.[1] During the formation of organogels or hydrogels, various chiral nanostructures were obtained through the self-assembly of small molecules by various noncovalent interactions, such as hydrogen bonding, π–π stacking, hydrophobic interactions, electrostatic interactions, metal ion to ligand coordination and so forth.[2] Even though some achiral gelators can assemble into chiral supramolecular nanostructures upon gelation, the gels are essentially a mixture of both left- and right-handed helices in equal amounts and thus overall racemic, showing no macroscopic optical activity, that is, they are CD silent.[3]

C_3-symmetric molecules, especially benzene-1,3,5-tricarboxamide derivatives, are important and versatile supramolecular building blocks.[4] Many of them are good gelators,[5] and their self-assembly properties have been explored as well.[6] In particular, symmetry breaking of self-assembled, achiral partially fluorinated benzene-1,3,5-tricarboxamides in solution was detected and analyzed.[7] Here, we show the formation of chiral assemblies from an achiral and C_3-symmetric benzene-1,3,5-tricarboxamide containing three identical ethyl cinnamate arms (BTAC) through supramolecular gelation. The chiral nanostructures could be clearly observed by scanning electron microscopy (SEM). The molecular structure of BTAC with the relatively large and rigid ethyl cinnamate substituents in peripheral positions probably results in an overcrowded environment during stacking,[8] thus leading to an uneven symmetry breaking and the formation of chiral assemblies (Scheme 1).

BTAC is soluble in various organic solvents (Table S1), and when water was added to a solution of BTAC in *N*,*N*-dimethylformamide (DMF), white gels were formed quickly at room temperature. The gels transformed into a solution upon heating and formed again after cooling (Figure S1). The UV-Vis spectra of BTAC gels and BTAC solutions with different concentrations were measured (Figure S2), and the broadened absorption peaks of the gels suggest a π–π stacking of BTAC molecules during the self-assembly. Most interestingly, although the gels in DMF/H_2O mixture were constructed from achiral BTAC, the CD spectra of the gels obtained from different batches clearly showed a significant positive or negative Cotton effect at 409 nm (Figure 1 a,b, mirror-imaged CD curves). Linear dichroism (LD) spectra of the gels were also measured to estimate the contribution from the LD effect to the CD spectra (Figure S3). The results show that the contamination of the CD spectra by LD artifacts was negligible. In order to quantitatively study the supramolecular chirality, the statistic distributions of the CD intensity at

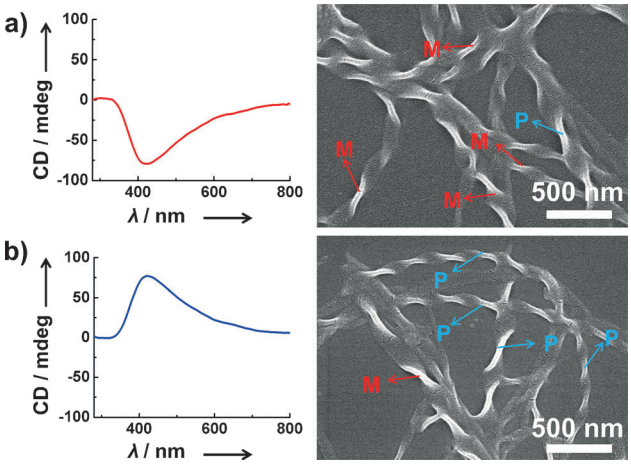

Figure 1. CD spectra and SEM images of optically active gels formed from BTAC in DMF/H_2O ($v/v = 5/2$). a) When the *M* twists outnumber the *P* twists, the CD spectrum shows a negative Cotton effect. b) When the *P* twists outnumber the *M* twists, the CD spectrum shows a positive Cotton effect.

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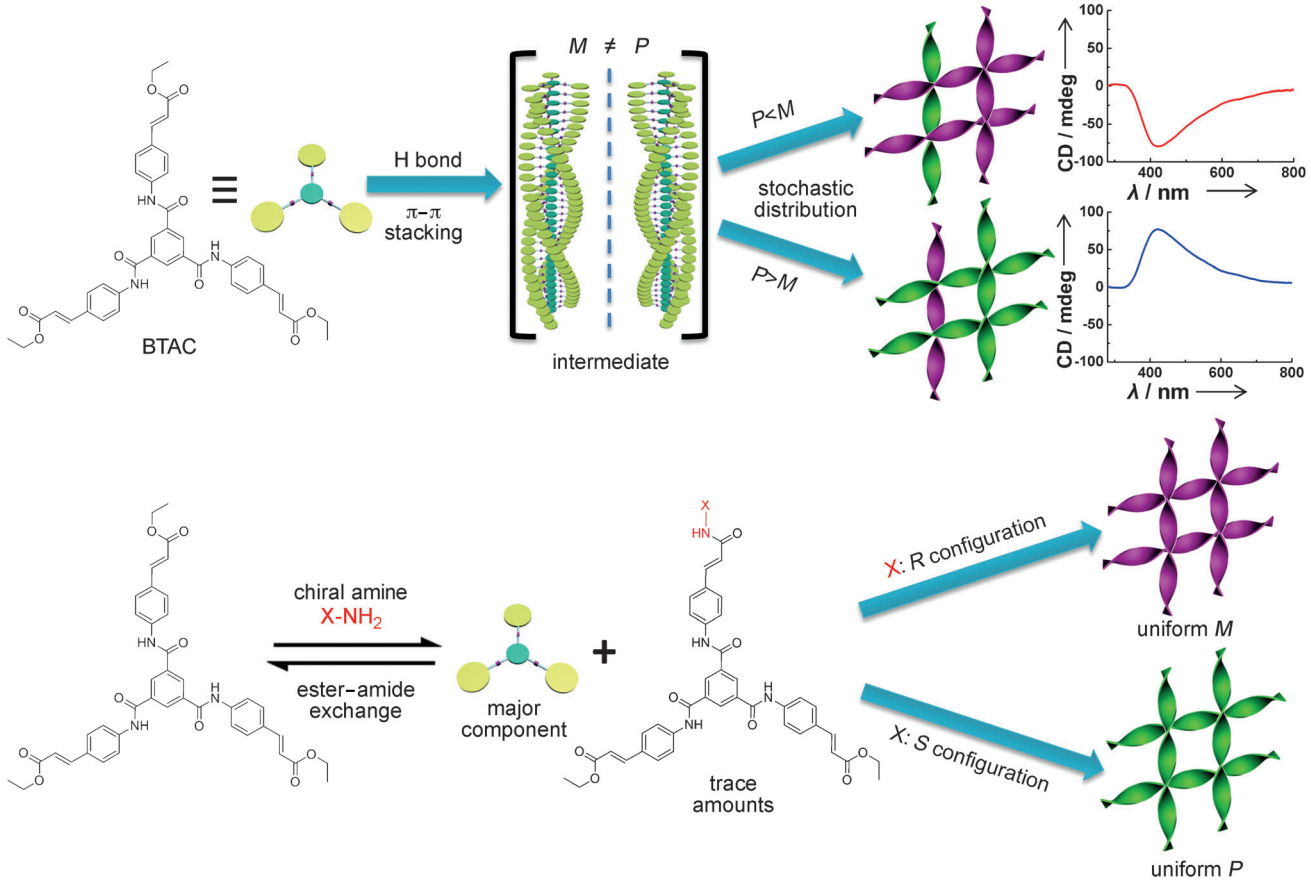


Scheme 1. Formation of optically active supramolecular gels by the hierarchical self-assembly of achiral BTAC building blocks, and control of supramolecular chirality through doping with chiral amines.

409 nm obtained from 100 samples was analyzed (Figure S4). A positive CD effect was detected from 48 samples, while the remaining 52 samples showed a negative CD effect, thus indicating that the sign of chirality is random.[9]

The optical activity and the supramolecular chirality of the assemblies was also shown by SEM (Figure 1 a,b). The gels from different batches showed left- (*M*) or right-handed (*P*) twists, the length of which was about ten micrometers. Furthermore, the SEM images showed uneven numbers of *M* and *P* twists, one of which was usually the dominant morphology. The relationship between the handedness of the twists and the CD signs could also be established. When the *M* twists outnumbered the *P* twists (Figure 1 a), the CD spectra always showed a negative Cotton effect (Figure 1 a); when the *P* twists outnumbered the *M* twists (Figure 1 b), the CD spectra showed a positive Cotton effect (Figure 1 b). These results suggest that an uneven symmetry breaking occurred during the self-assembly process, thus leading to the macroscopic chirality of the gels prepared from achiral BTAC molecules. However, different from the chiral thin films assembled from achiral amphiphiles at an air/water interface,[10] the optically active supramolecular gels were prepared in very large quantities by simply adding water to a solution of BTAC in DMF, which could be very useful for further applications.

The nanostructures of the optically active gels were strongly dependent on the conditions of the BTAC self-assembly. Although BTAC could self-assemble into diverse nanostructures in different solvents (Figure S5), none of these assemblies showed clear helices, not to mention optical activity. Uneven symmetry breaking was only observed in a DMF/H_2O mixture. Furthermore, both the concentration of BTAC and the volume ratio of the DMF/H_2O mixture had to be chosen carefully to obtain optically active gels. At a BTAC concentration of 15 mg mL^{-1} in DMF, helical assemblies could only be detected at a DMF/H_2O ratio of 5:2 (Figure S6), although supramolecular gels were formed at DMF/H_2O ratios between 5:2 to 5:4. SEM images of gels with different concentrations of BTAC in DMF/H_2O = 5:2 suggested that 15 mg mL^{-1} is the best concentration for the formation of twists. The G value,[2i] which indicates the ratio of the CD signal to the UV-Vis absorbance as a function of the concentration, also confirmed that BTAC gels formed at a concentration of the 15 mg mL^{-1} have the highest optical activity (Figure S7).

In order to further investigate the symmetry breaking in these gels, X-ray diffraction (XRD), FT-IR, and ^{1}H NMR measurements were performed. For BTAC assemblies, the threefold intermolecular hydrogen bonding from the amide moieties can be clearly identified from the FT-IR spectra, with one amide at 1658 cm^{-1} and the other amide at 1530 cm^{-1}

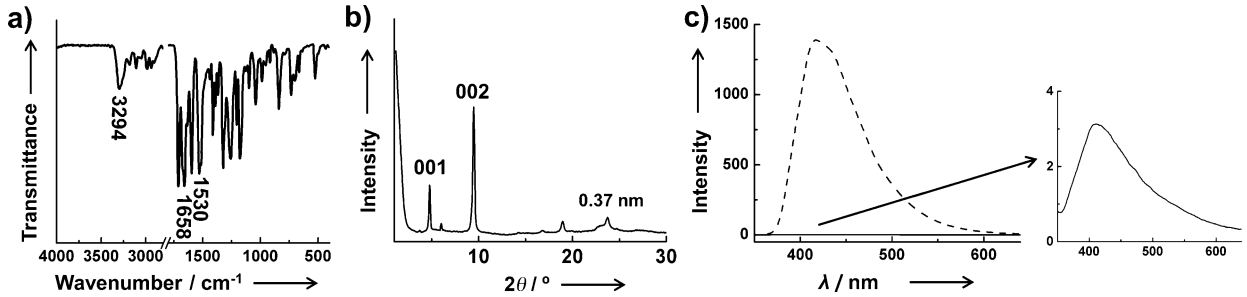


Figure 2. a) FT-IR spectrum and b) XRD pattern of BTAC gels in DMF/H_2O ($v/v = 5/2$). c) Fluorescence emission spectra of BTAC 1 % wt/vol gel in DMF/H_2O ($v/v = 5/2$) (dotted line) and DMF only with the same concentration (solid line) excited at 330 nm.

(Figure 2a). Evidence for amide hydrogen bonding was also obtained from ^{1}H NMR titration. When D_2O was slowly added to a solution of BTAC in [D_7]DMF, the chemical shifts of the amide protons on BTAC moved downfield, suggesting an enhancement of the hydrogen bonding interactions during the self-assembly process (Figure S8). Figure 2b shows the XRD pattern of BTAC gels in DMF/H_2O = 5:2. Two strong diffraction peaks were observed at 2θ values of 4.76 and 9.43, indicating the formation of a lamellar nanostructure in the twisted ribbons with an interlayer distance of 1.84 nm. In addition, a wide-angle peak at a 2θ value of 23.27 corresponds to a distance of 0.37 nm between two neighboring molecular planes in BTAC, suggesting a close stacking of the molecules. Moreover, the significant fluorescence enhancement during the gelation also indicates the tight molecular packing within the twists, as shown in fluorescence excitation spectra (Figure S9) and fluorescence emission spectra (Figure 2c) of the BTAC gels and solutions. When water was added to the solution of BTAC in DMF, the intensity of the fluorescence increased by a factor of about 400 (Figure 2c). In theory, this fluorescence enhancement of the supramolecular gels could be attributed to the fixed arrangement of the gelators.[11] In BTAC assemblies, only a congested packing can minimize the movement of molecules or restrict the intramolecular bond rotation and result in a significant fluorescence enhancement. These results demonstrate the multiple intermolecular interactions and tight molecular packing of different achiral BTAC molecules during the formation of optically active gels.

Based on the experimental data, a possible mechanism of symmetry breaking was established (Scheme 1). At the early stages of gelation, some of the BTAC molecules by chance assemble into one-dimensional helical aggregates with predominantly *P* or *M* conformation through the threefold intermolecular hydrogen bonding and π–π stacking. Once the helical aggregation with a certain handedness starts, the helical aggregates grow with the original chiral conformation because of the steric hindrance resulting from the overcrowded molecular packing. The hierarchical self-assembly of these small helical nanostructures further produces larger twisted ribbons[12] with an unequal amount of *P* and *M* conformations. Indeed, only special achiral molecules, such as BTAC, can self-assemble into optically active supramolecular gels with chiral nanostructures. Thus, uneven symmetry breaking and the macroscopic optical activity can be observed, similar to getting supramolecular chirality from achiral molecular building blocks through assembly at an air/water interface.[10]

The chirality of supramolecular assemblies can be controlled by chiral dopants[13] and rotary stirring.[14] Interestingly, the macroscopic chirality of BTAC gels and the handedness of the twists can also be controlled by introducing chiral dopants. For example, adding chiral 1-cyclohexyl ethylamine to the gels controlled the handedness of the twisted ribbons and thus the direction of CD signs. For the BTAC gels containing (*R*)-1-cyclohexyl ethylamine with a molar ratio of BTAC/amine = 1:3, a strong CD signal with an exciton-type Cotton effect at 409 nm and a crossover at 330 nm was detected (Figure 3c). Moreover, only *M* twists were observed from the SEM image (Figure 3a). In contrast, in the case of BTAC gels containing (*S*)-1-cyclohexyl ethylamine, the mirror-imaged CD spectrum and *P* twists were observed (Figure 3b). As amines can interact with ethyl cinnamate,[15] a small number of chiral amines may react with ethyl cinnamate through an ester–amide exchange reaction and connect with BTAC through covalent binding. Indeed, the portion of BTAC/amine complexes is very small, so it

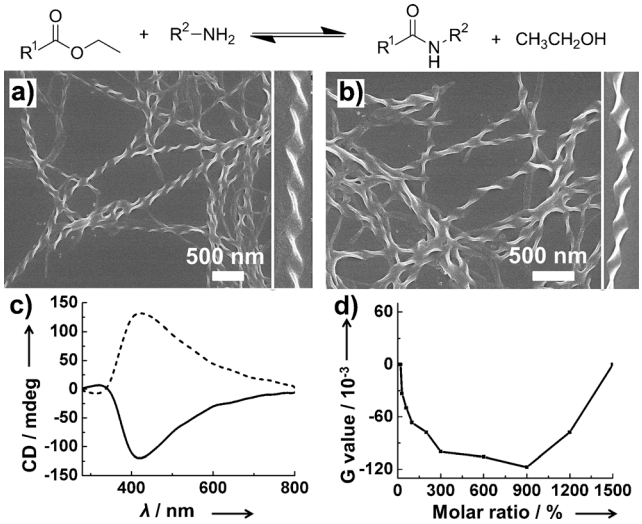
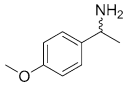


Figure 3. SEM images of the BTAC gels containing 300 mol% 1-cyclohexyl ethylamine with a) *R* or b) *S* configuration. c) CD spectra of the BTAC gels containing 300 mol% 1-cyclohexyl ethylamine with *R* (solid line) or *S* (dotted line) configuration. d) G values of BTAC gels at 409 nm as a function of the molar ratio of (*R*)-1-cyclohexyl ethylamine/BTAC.

cannot be detected by NMR spectroscopy. However, macroscopic chirality of the optically active gels containing chiral amines with a certain configuration kept constant after most of the doped chiral amines were removed from the system through vacuum drying, as confirmed by CD and NMR spectral measurements (Figure S10). These results support the hypothesis that a small number of chiral amines reacted with the ethyl cinnamate moieties, forming covalent bonds.

For controlling the macroscopic chirality of BTAC gels, the molar ratio of BTAC/chiral amines is very important. In general, a higher content of chiral (*R*)-1-cyclohexyl ethylamine in the system resulted in a higher macroscopic chirality (Figure 3d). However, if the content of chiral (*R*)-1-cyclohexyl ethylamine became too high, gelation was inhibited and optically active gels were not obtained (Figure S11). Although additional chiral (*R*)-1-cyclohexyl ethylamine can give larger G values, 30 mol% is enough to control the macroscopic chirality of BTAC gels (Table 1). For other chiral

Table 1: Minimum content of selected chiral amines in BTAC gels for successfully controlling the macroscopic chirality.

Amines				
Content [mol%]	30	30	60	–

amines, such as 1-(4-methoxyphenyl) ethylamine, which contains an aromatic ring, and *sec*-butylamine with its very low molecular weight, the control of the macroscopic chirality of BTAC gels was also observed in the CD spectra and SEM images (Figure S12). Similarly, 30 mol% 1-(4-methoxyphenyl) ethylamine and 60 mol% sec-butylamine were sufficient to control the macroscopic chirality. Interestingly, the macroscopic chirality of BTAC gels can not be controlled with 1,2-diaminocyclohexane, which contains two chiral centers. Even though a large quality of (*R*,*R*) or (*S*,*S*)-1,2-diaminocyclohexane was added to the system, positive or negative CD signs were always distributed stochastically.

In conclusion, the steric hindrance of ethyl cinnamate substituents resulted in the self-assembly of an achiral and C_3-symmetric molecule (BTAC) into an unequal number of *P* and *M* twists and the formation of optically active supramolecular gels with macroscopic chirality. Moreover, the handedness of the twists could be linked with the macroscopic chirality of the BTAC gels, and controlled successfully by a small amount of chiral amines through amide–ester exchange reaction. This is the first study demonstrating that a C_3-symmetric and achiral low-molecular-weight gelator can form optically active supramolecular gels with controllable macroscopic chirality. These findings provide evidence for the origin and control of chirality in supramolecular systems.

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