Supporting Information

Symmetry Breaking in the Supramolecular Gels of an Achiral Gelator Exclusively Driven by π–π Stacking

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1. Synthetic procedures

The methyl cinnamate-substituted benzenetriester (BTECM) was prepared by treating 1, 3, 5-benzenetricarbonyl trichloride with methyl 4-hydroxycinnamate as shown in Scheme S1. A THF solution (10 mL) of 1,3,5-benzenetricarbonyl trichloride (0.53 g, 2.0 mmol) was added to a solution containing methyl 4-hydroxycinnamate (1.43 g, 8.0 mmol) and triethylamine (2.2 mL, 16.0 mmol) in 20 mL THF. The resulting mixture was stirred at room temperature for 12 hours and filtered. The filtrate was concentrated by rotary evaporation and 50 mL methanol was added to the residue. The solid precipitate was filtered, followed by washing on the filter paper consecutively with water (20 mL) and methanol (20 mL). This clean product was dried to give a white powder.

The ethyl/n-propyl/n-butyl cinnamate-substituted benzenetriester (BTECE/BTECP/BTECB) were prepared with the above method except that methyl 4-hydroxycinnamate was replaced by ethyl/n-propyl/n-butyl 4-hydroxycinnamate. n-Propyl/n-butyl 4-hydroxycinnamate were synthesized according to previously reported procedure (*Tetrahedron: Asymmetry* **1996**, *7*, 2863-2870).

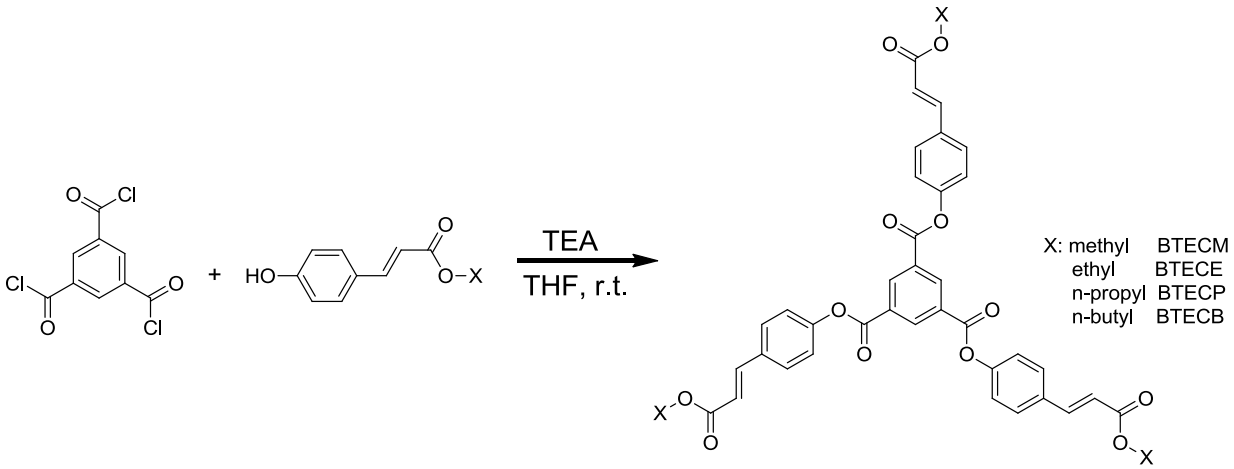
BTECM, yield = 83%. ^{1}H NMR (400 MHz, d_6-DMSO, δ, ppm): 3.74 (s, 9H, CH_3), 6.67-6.71 (d, 3H, CH), 7.45-7.47 (d, 6H, Ar-H), 7.70-7.74 (d, 3H, CH), 7.87-7.89 (d, 6H, Ar-H), 9.04 (s, 3H, Ar-H). MALDI-TOF MS: calcd. for $C_{39}H_{30}O_{12}$ M^+: m/z = 690.65; found $[M+Na]^+$: m/z = 713.3. Elemental Analysis: calcd. for $C_{39}H_{30}O_{12}$: C 67.82, H 4.38; found: C 67.75, H 4.35.

BTECE, yield = 67%. ^{1}H NMR (400 MHz, d_6-DMSO, δ, ppm): 1.26-1.28 (t, 9H, CH_3), 4.18-4.23 (m, 6H, CH_2), 6.66-6.70 (d, 3H, CH), 7.44-7.46 (d, 6H, Ar-H), 7.69-7.72 (d, 3H, CH), 7.86-7.89 (d, 6H, Ar-H), 9.03 (s, 3H, Ar-H). MALDI-TOF MS: calcd. for $C_{42}H_{36}O_{12}$ M^+: m/z = 732.73; found $[M+Na]^+$: m/z = 755.3. Elemental Analysis: calcd. for $C_{42}H_{36}O_{12}$: C 68.85, H 4.95; found: C 68.58, H 5.00.

BTECP, yield = 66%. ^{1}H NMR (400 MHz, d_6-DMSO, δ, ppm): 0.92-0.97 (t, 9H, CH_3), 1.61-1.73 (m, 6H, CH_2),4.10-4.14 (t, 6H, CH_2), 6.66-6.72 (d, 3H, CH), 7.45-7.48 (d, 6H, Ar-H), 7.68-7.74 (d, 3H, CH), 7.87-7.90 (d, 6H, Ar-H), 9.04 (s, 3H, Ar-H). MALDI-TOF MS: calcd. for $C_{45}H_{42}O_{12}$ M^+: m/z = 774.27; found $[M+Na]^+$: m/z = 797.3. Elemental Analysis: calcd. for $C_{45}H_{42}O_{12}$: C 69.76, H 5.46; found: C 69.45, H 5.42.

BTECB, yield = 74%. ^{1}H NMR (400 MHz, d_6-DMSO, δ, ppm): 0.90-0.95 (t, 9H, CH_3), 1.32-1.45 (m, 6H, CH_2), 1.59-1.68 (m, 6H, CH_2),4.14-4.19 (t, 6H, CH_2), 6.65-6.71 (d, 3H, CH), 7.44-7.47 (d, 6H, Ar-H), 7.67-7.73 (d, 3H, CH), 7.87-7.90 (d, 6H, Ar-H), 9.03 (s, 3H, Ar-H). MALDI-TOF MS: calcd. for $C_{48}H_{48}O_{12}$ M^+: m/z = 816.31; found $[M+Na]^+$: m/z = 839.3. Elemental Analysis: calcd. for $C_{48}H_{48}O_{12}$: C 70.57, H 5.92; found: C 70.53, H 5.97.

Scheme S1. Synthesis of BTECM, BTECE, BTECP, and BTECB.



2. Supplementary figures

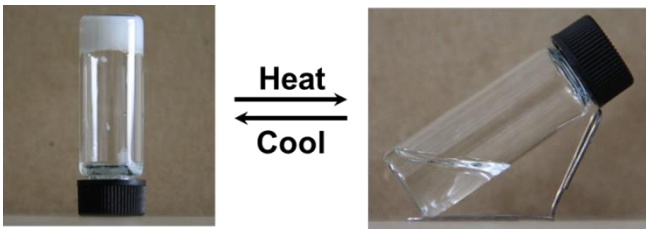


Figure S1. Photographs of the white gels formed by BTECM in ethanol (0.3% w/v) and the reversible gel-sol transition by temperature.

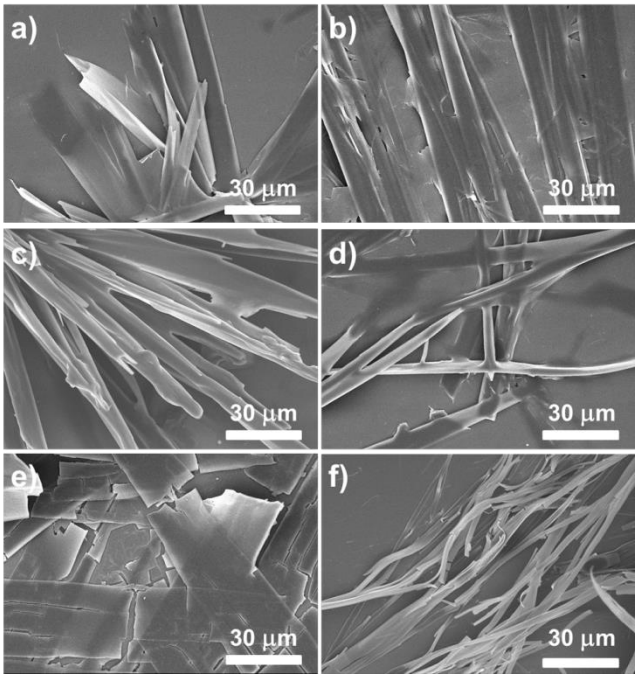


Figure S2. SEM images of the BTECP and BTECB precipitates (0.3% w/v) in various solvents: (a) BTECP in ethanol, (b) BTECB in ethanol, (c) BTECP in methanol, (d) BTECB in methanol, (e) BTECP in cyclohexane, and (f) BTECB in cyclohexane.

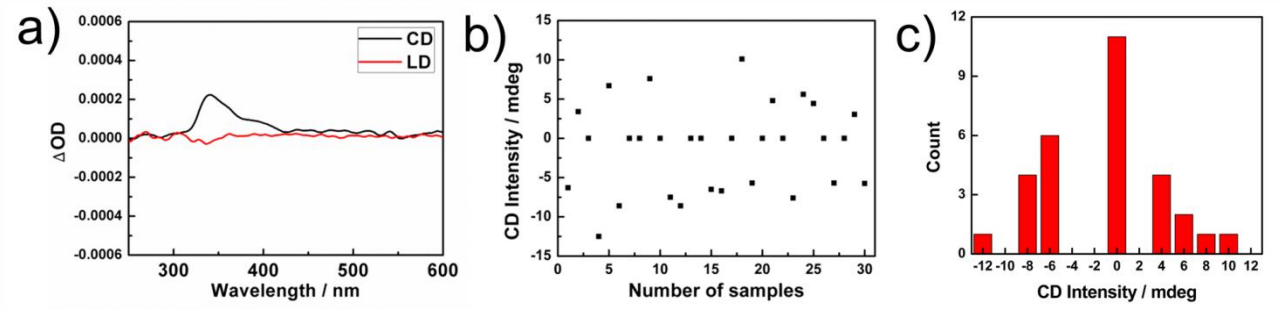


Figure S3. (a) CD and LD spectra of BTECM gels in cyclohexane (0.2% w/v), which are unified as the same unit (ΔOD). (b) The statistical distribution of the handedness and intensity of the CD signals around 340nm from 30 samples of BTECM gels in cyclohexane (0.2% w/v). (c) Histogram of CD intensity for 30 samples.

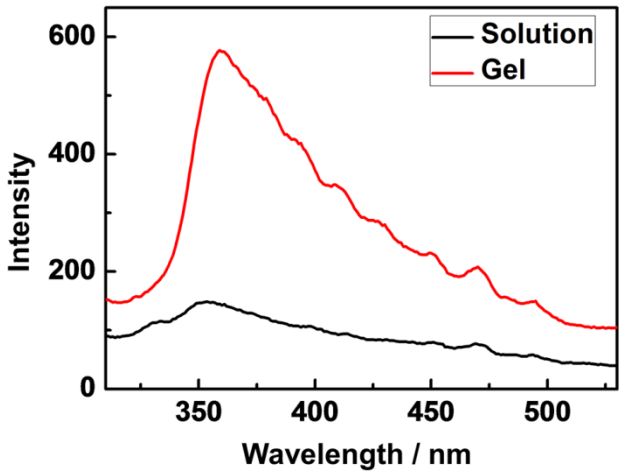


Figure S4. Fluorescence emission spectra of BTECM: 0.2% w/v gel in cycohexane (red curve) and hot solution with the same concentration (black curve). λ_{ex} = 290 nm.

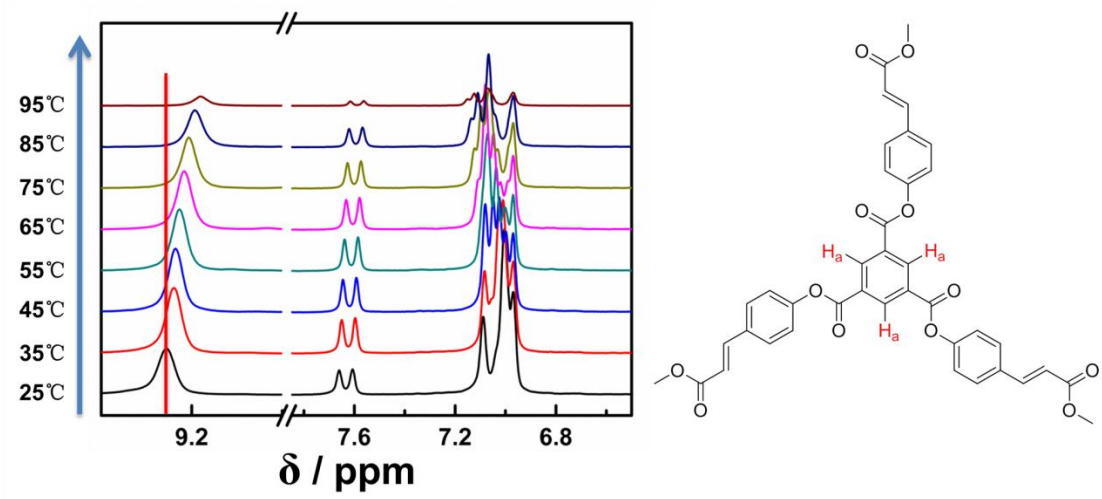


Figure S5. Temperature-dependent ^{1}H NMR spectra of BTECM in d_8-toluene (5 mg mL^{-1}).

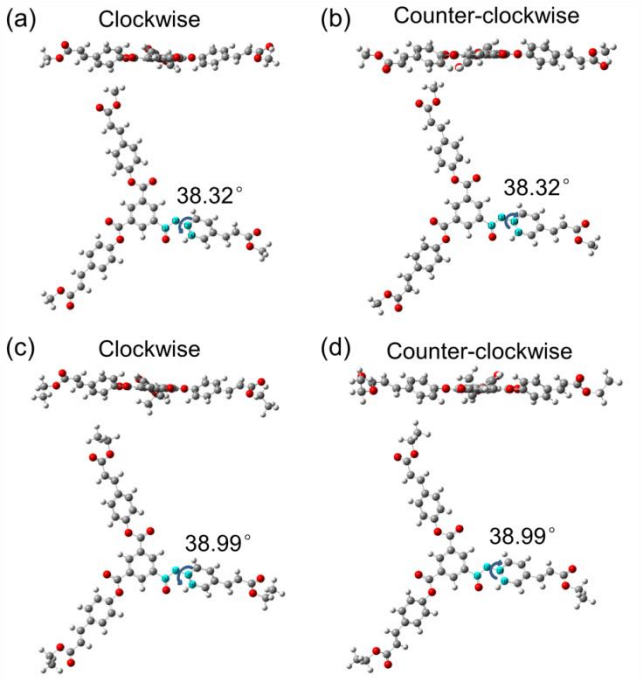


Figure S6. The two equilibrium conformations for achiral BTECM (a, b) and BTECE (c, d) molecules.

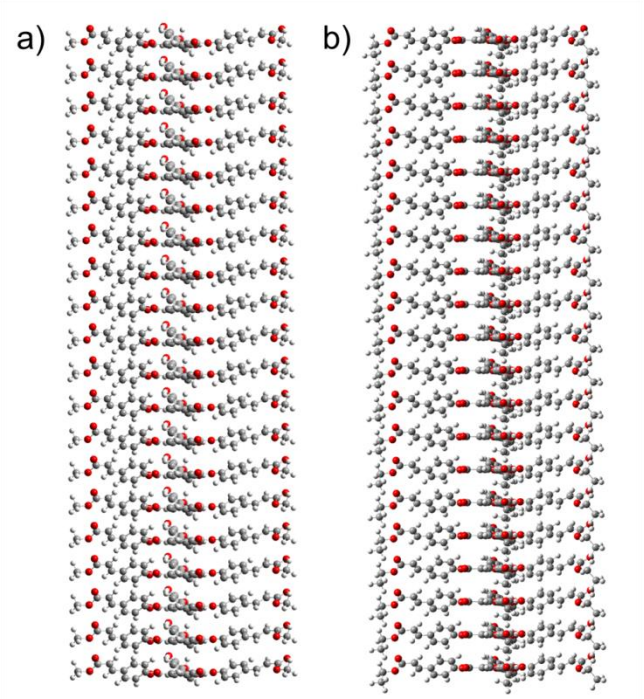


Figure S7. The preassembly aggregates of BTECM (a) and BTECE (b) containing 20 molecules.

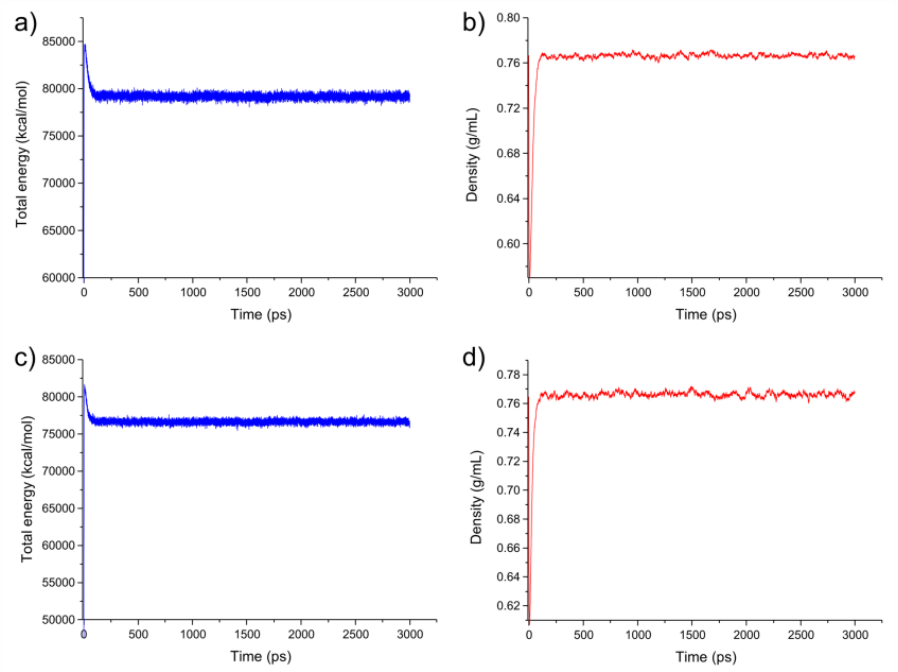


Figure S8. The total energy and density as a function of time for BTECM (a, b) and BTECE (c, d) systems.

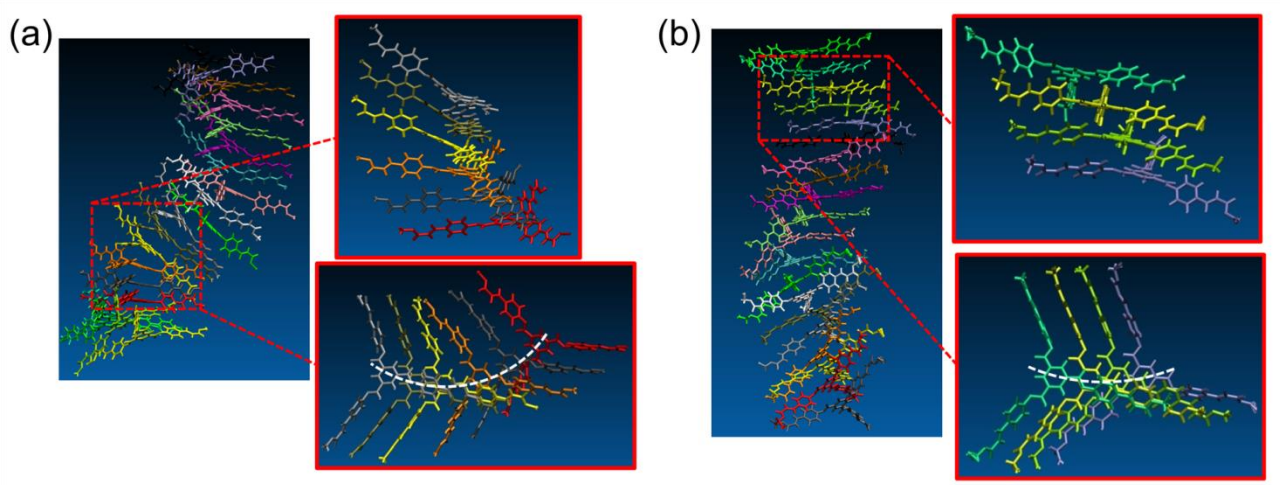


Figure S9. The average configurations of BTECM (a) and BTECE (b) aggregates after 200 ps of dynamics. The dashed boxes have been enlarged on their right sides.

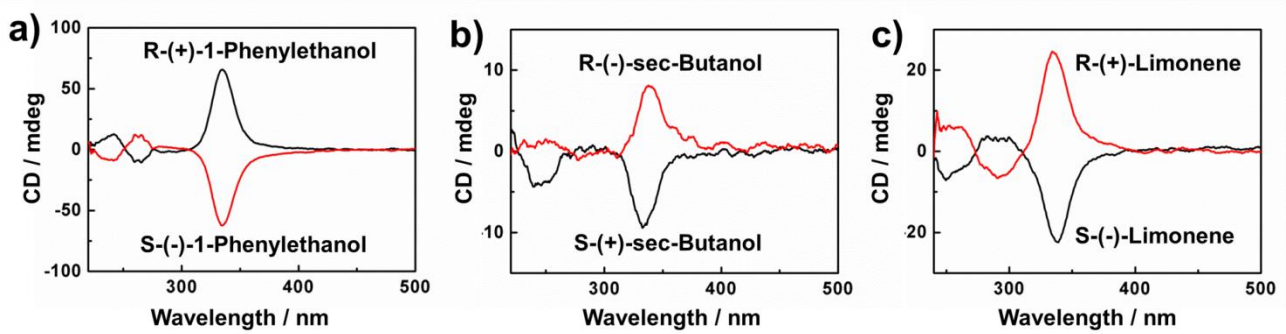


Figure S10. CD spectra of the BTECM gels (0.2% w/v) containing 1-phenylethanol (a), sec-butanol (b) and limonene (c) with volume ratios of chiral solvents/(cyclohexane + chiral solvents) equal to 0.05, 0.1 and 0.2, respectively.

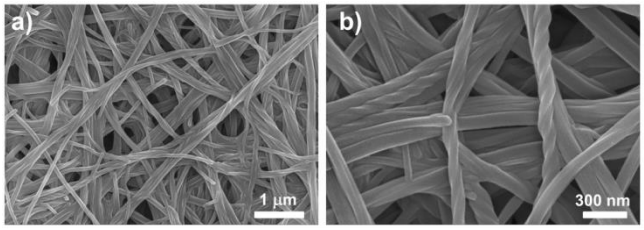


Figure S11. SEM images of the partial gels formed by BTECM (0.2% w/v) in cyclohexane with volume ratio of terpinen-4-ol/(cyclohexane + terpinen-4-ol) equal to 0.5.

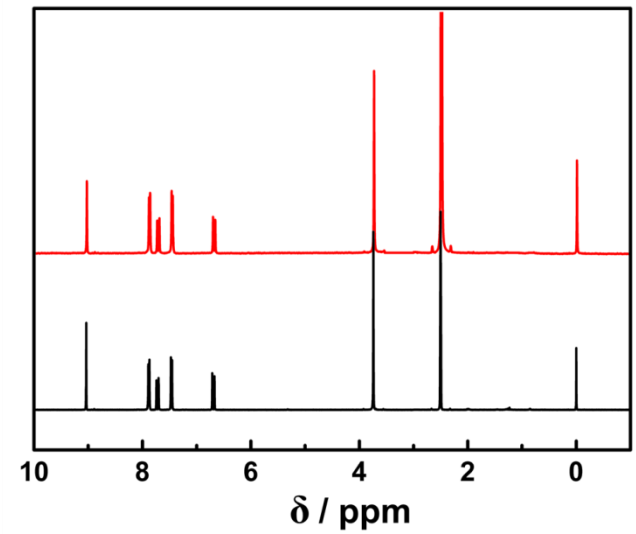


Figure S12. ^{1}H NMR of BTECM powders (black curve) and BTECM xerogels after vacuum drying to remove the chiral solvents (red curve) in d_6-DMSO at room temperature.