Supporting Information for

Triple circularly polarized luminescence of phenylalanine-based supramolecular gels regulated by kinetic and thermodynamic assembly pathways

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1. Instruments and materials

Materials

All reagents and solvents were used as received or otherwise indicated. Methyl L- and D-phenylalaninate hydrochloride was purchased from MedBio and Acmec, respectively. Triethylamine was purchased from Acmec. 1,3,5-Benzenetricarbonyl chloride was purchased from Amethyst.

Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Fourier 300 (300 MHz) spectrometer. Infrared spectra were recorded with a JASCO FTIR-660 spectrometer. UV-vis and CD spectra were obtained using Hitachi U-3900 spectrophotometer and JASCO J-1500 spectrophotometers, respectively. Photoluminescence spectra of both the solution and gels were measured on an F-4500 fluorescence spectrophotometer using a Xenon lamp as the excitation source and CPL spectra were measured on JASCO CPL-300. X-ray diffraction (XRD) was performed on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with Cu/Kα radiation (λ=1.5406Å). Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 FE-SEM with an accelerating voltage of 10 kV. ESI-MS was performed on Bruker Daltonics micro TOF instrument. The rheological properties of the gels were measured at 25°C with a Discovery HR-30 rheometer.

2. Synthetic procedure and characterization

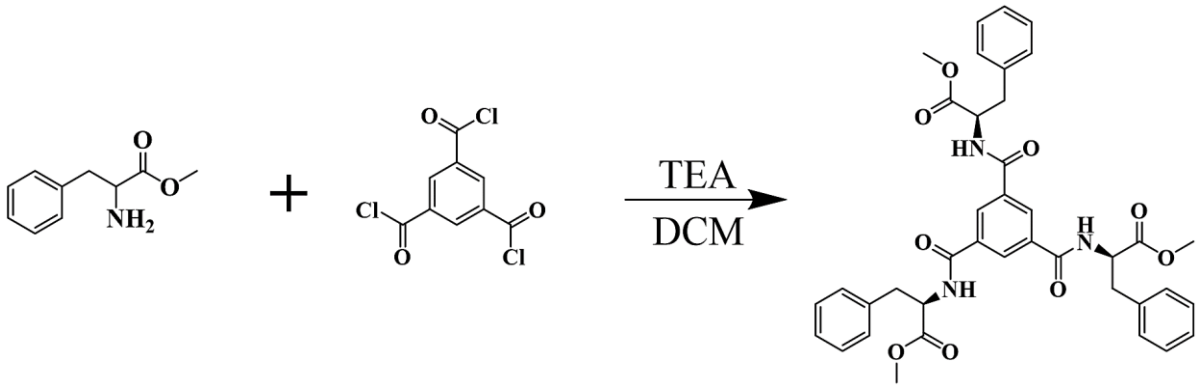

Fig. S1 Synthetic route of L-BTAFM.

1.73 g (8 mmol) of L-phenylalanine methyl ester hydrochloride was weighed and transferred into a round-bottom flask. To dissolve the compound, 30 mL of anhydrous dichloromethane was added. The flask was placed in an ice bath, and the solution was stirred while 2.2 mL of triethylamine was slowly added with continuous stirring. Separately, 0.531 g (2 mmol) of 1,3,5-benzenetricarbonyl chloride was weighed and dissolved in 10 mL of anhydrous dichloromethane in a beaker. This solution was gradually added dropwise to the round-bottom flask while stirring, and the reaction was allowed to proceed overnight. Upon completion of the reaction, the mixture was filtered to collect the filtrate, and the solvent was removed using rotary evaporation, yielding the crude product. The crude product was dissolved in ethanol and recrystallized three times, producing the final product, which weighed 1.13 g (1.6 mmol, 81%).

1.73 g (8 mmol) of D-phenylalanine methyl ester hydrochloride was weighed and transferred into a round-bottom flask. To dissolve the compound, 30 mL of anhydrous dichloromethane was added. The flask was placed in an ice bath, and the solution was stirred while 2.2 mL of triethylamine was slowly added with continuous stirring. Separately, 0.531 g (2 mmol) of 1,3,5-benzenetricarbonyl chloride was weighed and dissolved in 10 mL of anhydrous dichloromethane in a beaker. This solution was gradually added dropwise to the round-bottom flask while stirring, and the reaction was allowed to proceed overnight. Upon completion of the reaction, the mixture was filtered to collect the filtrate, and the solvent was removed using rotary evaporation, yielding the crude product. The crude product was dissolved in ethanol and recrystallized three times, producing the final product, which weighed 1.06 g (1.53 mmol, 76.4%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 3H), 7.30 (t, J = 7.1 Hz, 6H), 7.23 (d, J = 7.3 Hz, 2H), 7.17 (d, J = 6.6 Hz, 6H), 6.89 (d, J = 7.7 Hz, 3H), 5.10 – 5.03 (m, 3H), 3.77 (s, 9H), 3.32 – 3.17 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.52, 165.32, 136.15, 134.59, 129.21, 128.70, 128.54, 127.20, 54.29, 52.61, 37.83.

HR-MALDI-TOF-MS: calcd. for $C_{39}H_{39}N_3O_9$ M^+: m/z = 693.27; found $[M+H]^+$: m/z = 693.96, $[M+Na]^+$: m/z = 715.932.

3. Supplementary figures and tables

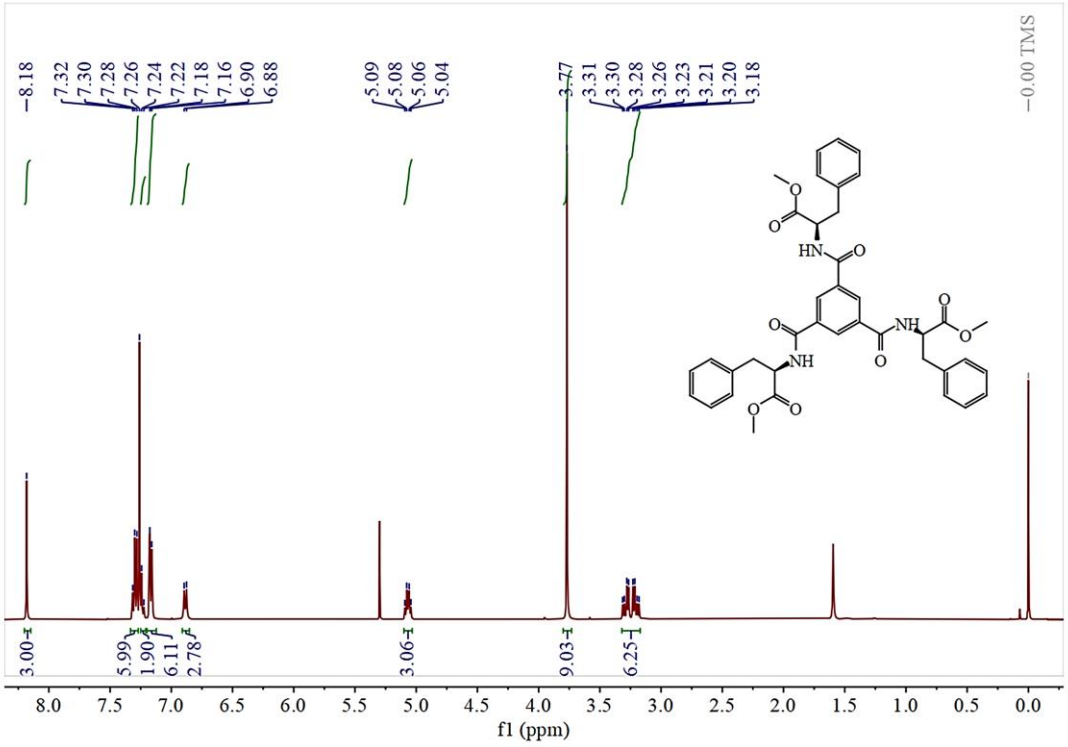

Fig. S2 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of L-BTAFM.

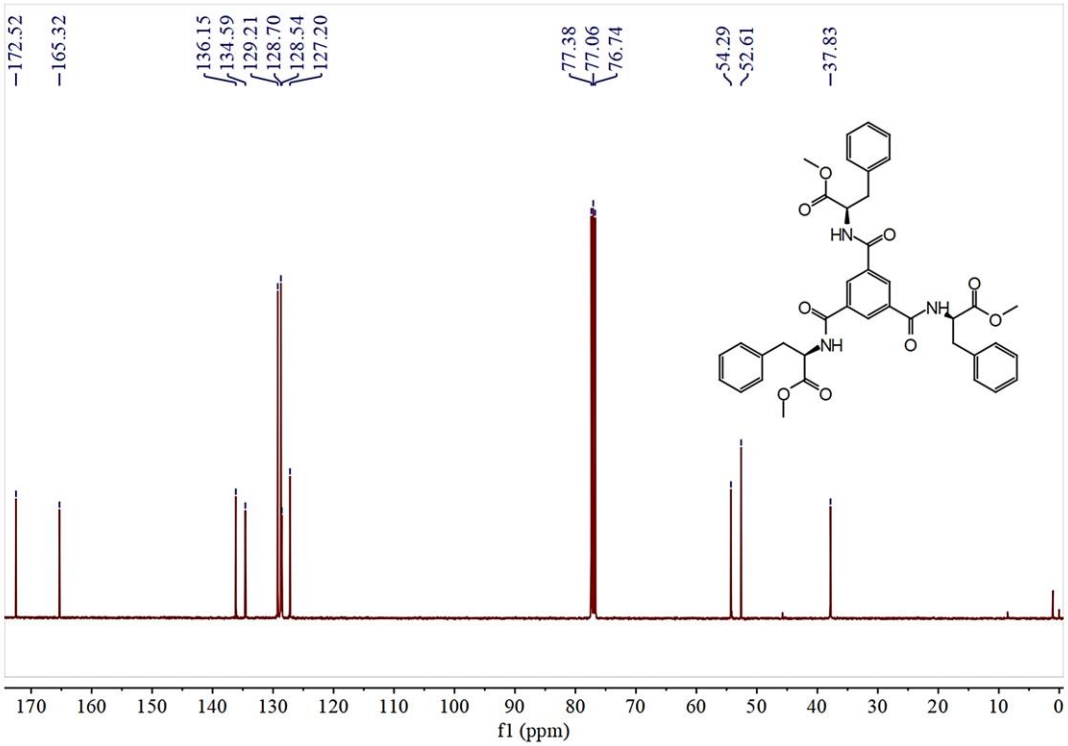

Fig. S3 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of L-BTAFM.

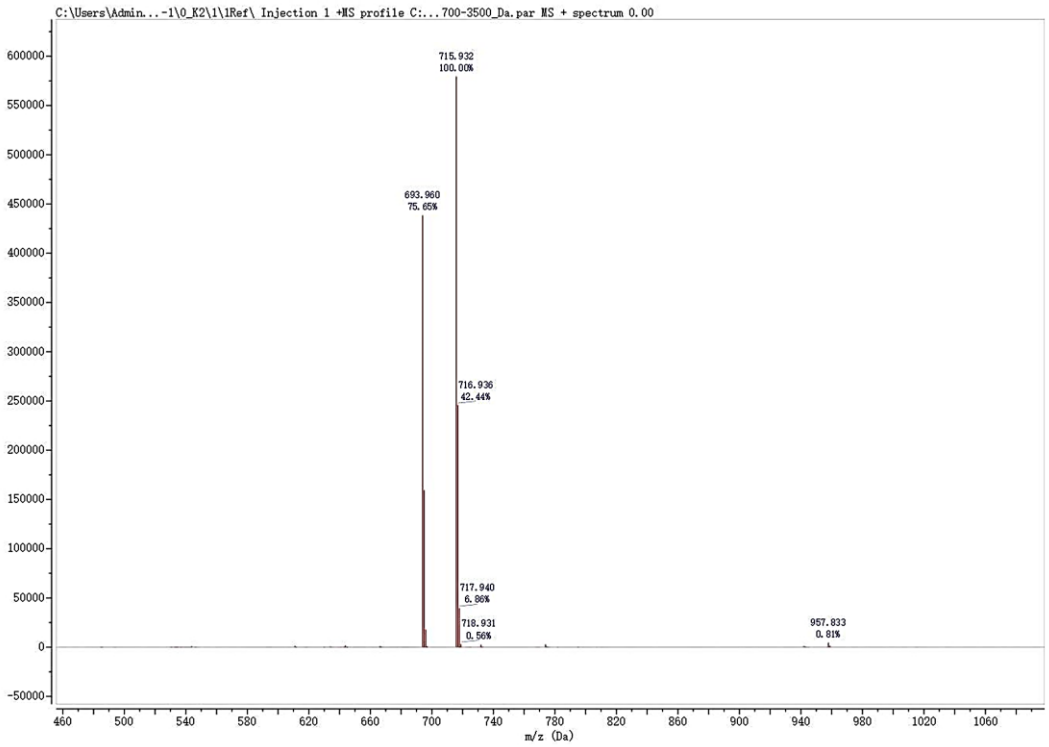

Fig. S4 HR-MALDI-TOF mass spectrum of L-BTAFM.

Table S1 Gelation behaviors of BTAFM in various solvents.

Solvent	Property	CGC (mM)
H_2O	I	——
Methanol	S	——
Ethanol	G	——
Acetone	S	——
THF	S	——
DMSO	S	——
DMF	S	——
$CHCl_3$	S	——
Ethyl acetate	G	——
CH_2Cl_2	S	——
Toluene	G	10
Cyclohexane	I	——
n-Hexane	I	——

G: stable gel; S: soluble; I: insoluble.

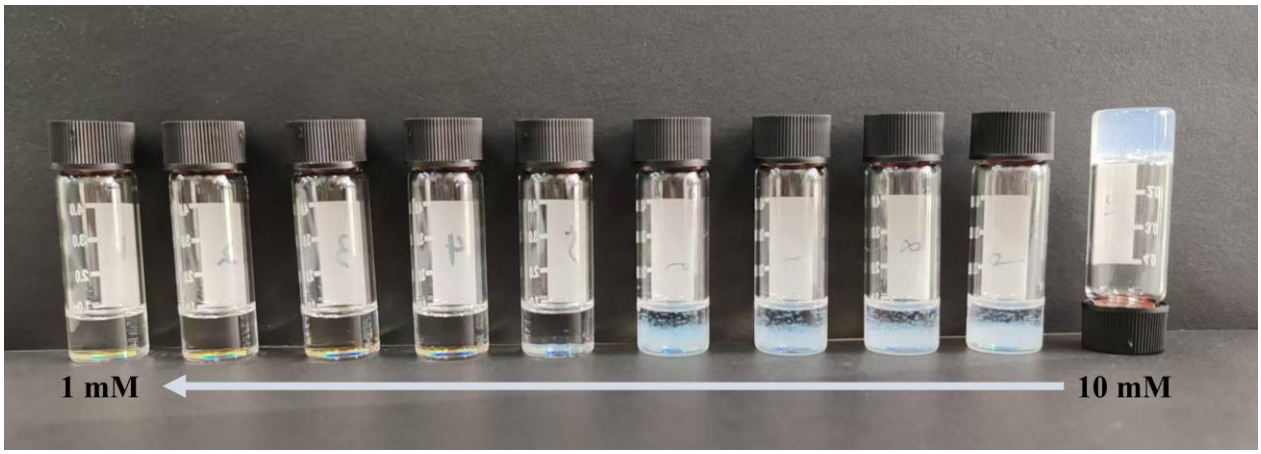

Fig. S5 a) Optical images of BTAFM samples in toluene at different concentrations after heating and cooling.

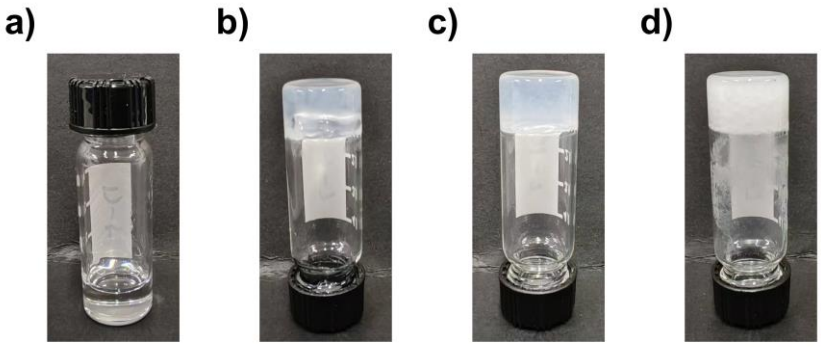

Fig. S6 a) Optical image of BTAFM solution (5 mM) in toluene after heating and cooling. **b)** Optical image of BTAFM gel (5 mM) in toluene after heating and cooling under ultrasound. **c)** Optical image of BTAFM gel (10 mM) in toluene after heating and cooling. **d)** Optical image of BTAFM gel (40 mM) in toluene after heating and cooling.

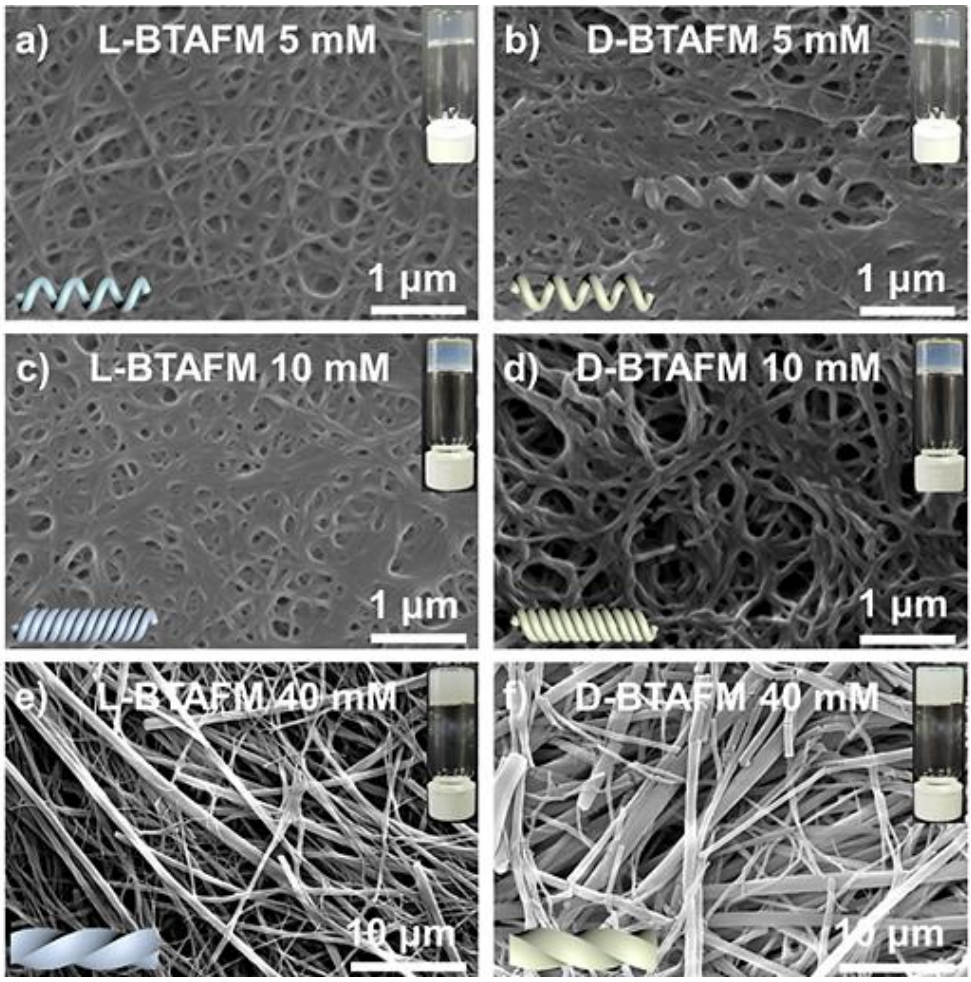

Fig. S7 SEM images of the dried samples of L- and D-BTAFM gels in toluene at different concentrations: **a, b)** 5 mM**, c, d)** 10 mM, **e, f)** 40 mM.

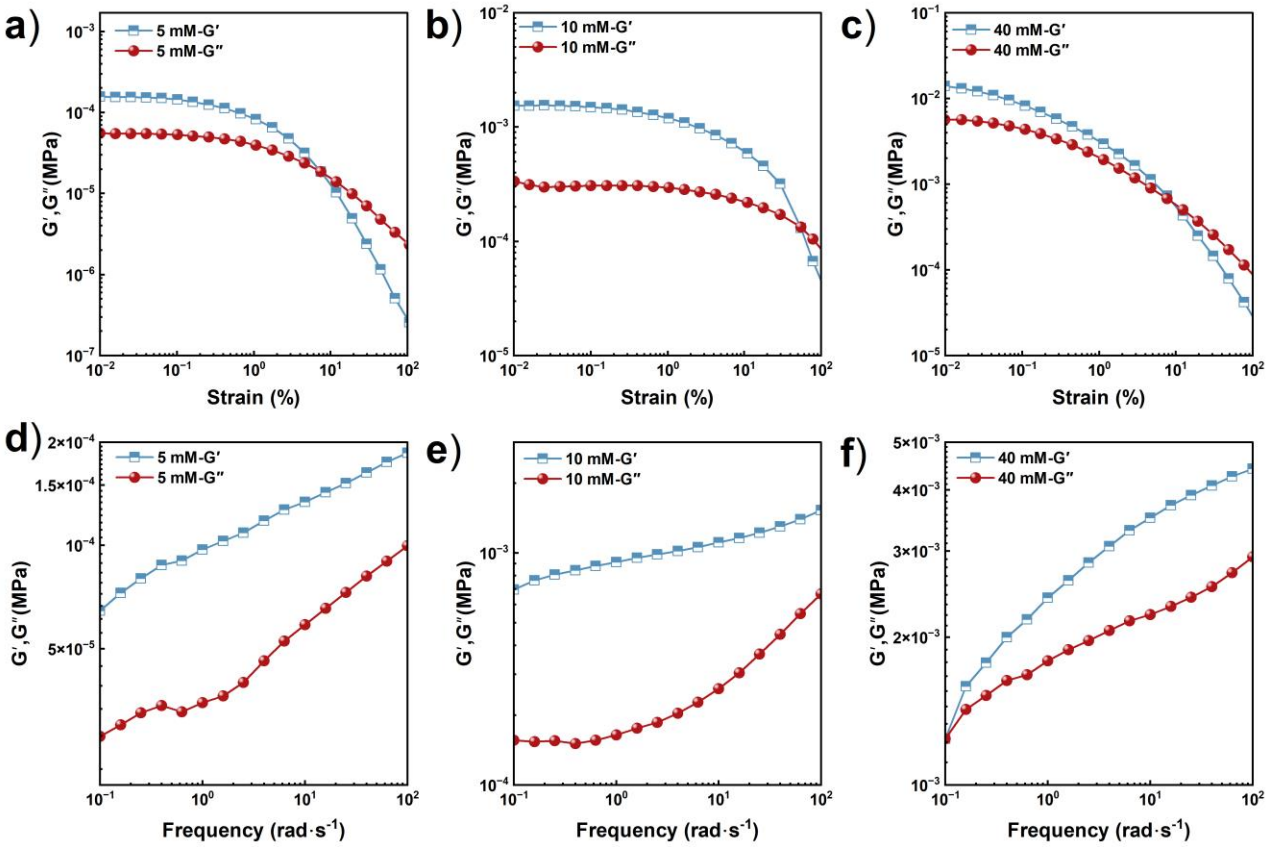

Fig. S8 a-c) Strain dependence of storage modulus G' and loss modulus G" of BTAFM gels in toluene at different concentrations performed at 25°C under a constant 10 rad s^{-1} frequency: **a)** 5 mM, **b)** 10 mM, and **c)** 40 mM. **d-f)** Frequency dependence of storage modulus G' and loss modulus G" of BTAFM gels in toluene at different concentrations performed at 25°C under a constant 0.5% strain: **d)** 5 mM, **e)** 10 mM, and **f)** 40 mM.

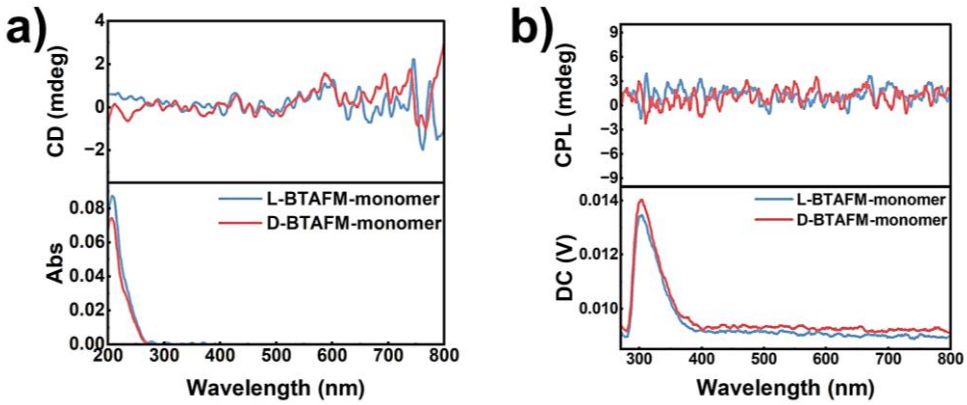

Fig. S9 a) CD and UV-vis spectra of L- and D-BTAFM solution (0.05 mM) in toluene. **b)** CPL spectra of L- and D-BTAFM solution (0.05 mM) in toluene excited at 258 nm.

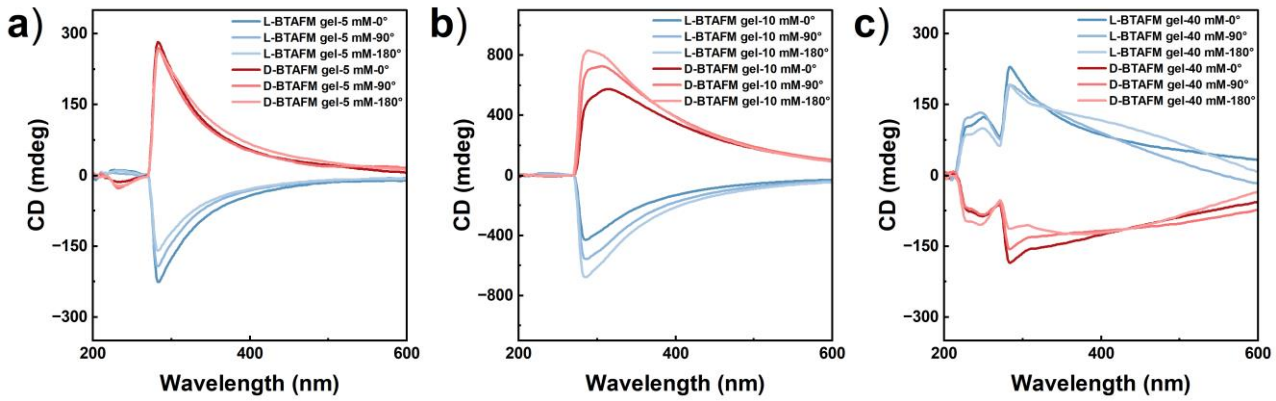

Fig. S10 CD spectra of BTAFM gels at different concentrations in toluene at angles of 0°, 90° and 180°: **a)** 5 mM, **b)** 10 mM, and **c)** 40 mM.

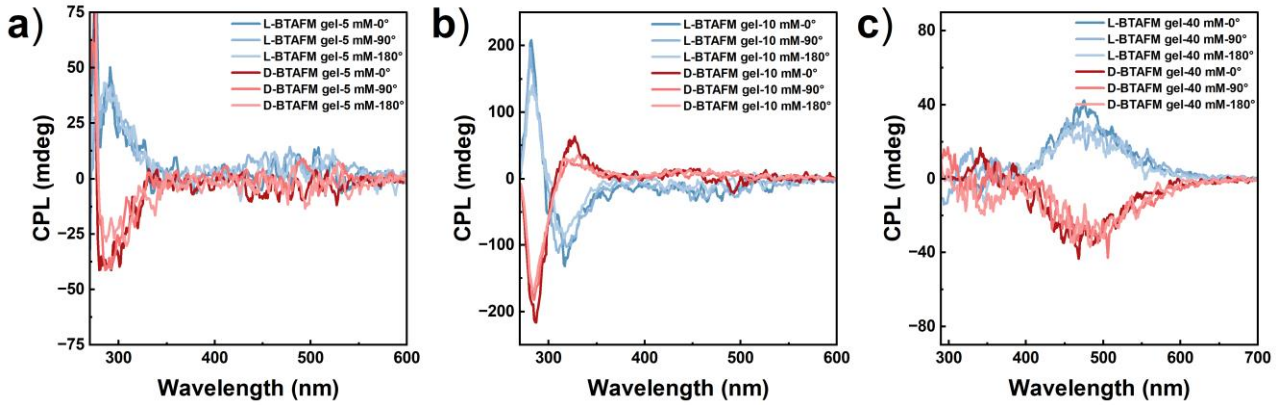

Fig. S11 CPL spectra of BTAFM gels at different concentrations in toluene at angles of 0°, 90° and 180°: **a)** 5 mM, **b)** 10 mM, and **c)** 40 mM.

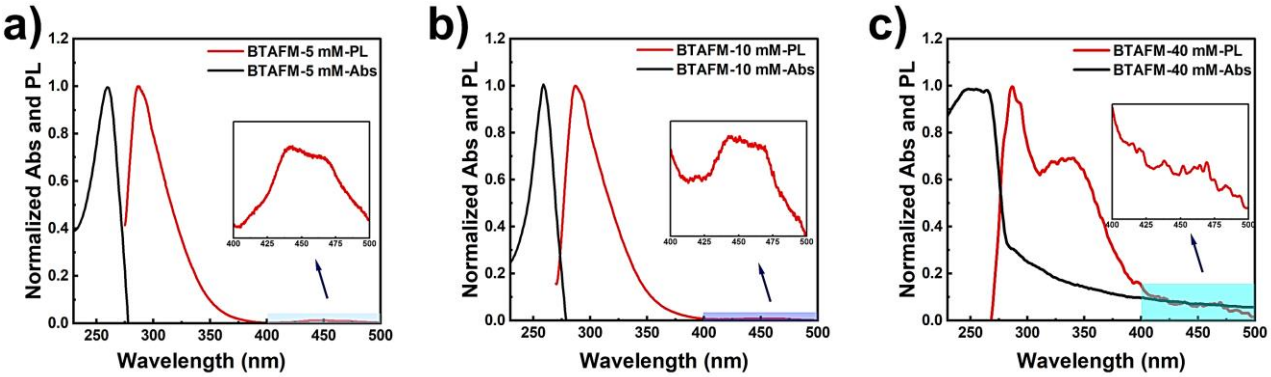

Fig. S12 Normalized absorption and photoluminescence spectra of BTAFM gels in toluene at different concentrations: **a)** 5 mM, **b)** 10 mM, and **c)** 40 mM. λ_{ex}=258 nm.

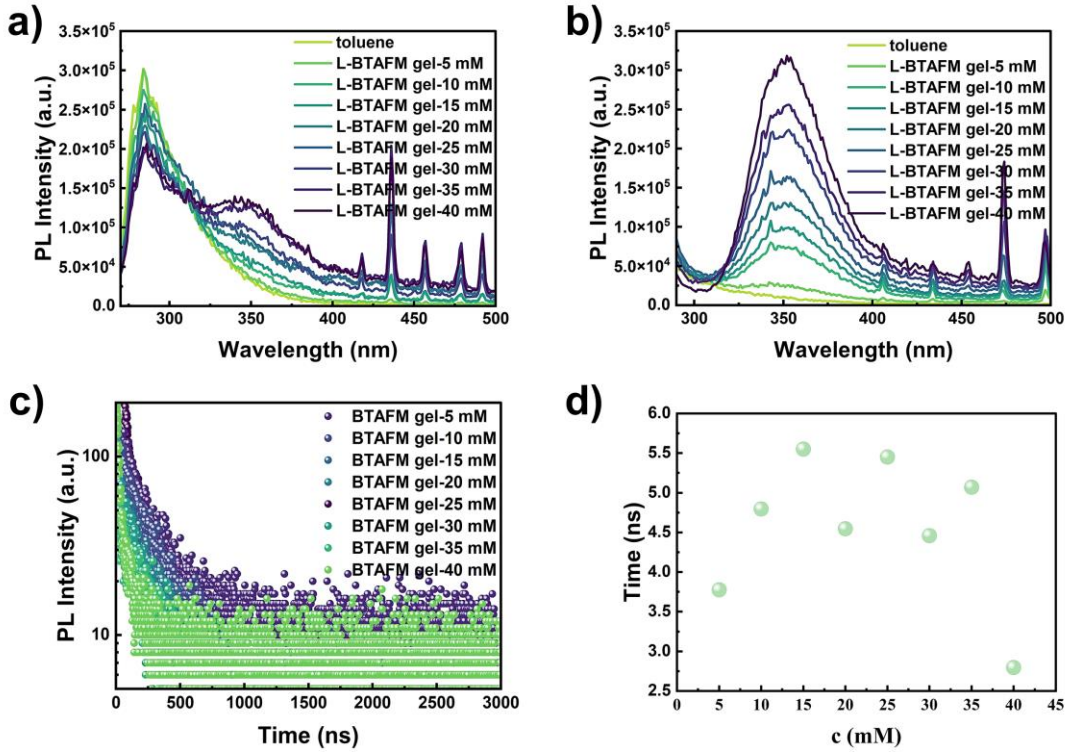

Fig. S13 a, b) Photoluminescence spectra of L-BTAFM gels at different concentrations (λ_{ex}=258 nm). **c)** FL decay curves at 340 nm for L-BTAFM gels at different concentrations (λ_{ex}=277 nm). **d)** Fluorescence lifetime at 340 nm for L-BTAFM gels at different concentrations.

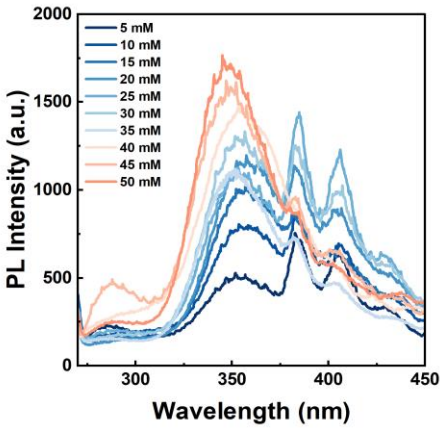

Fig. S14 Photoluminescence spectra of the xerogels obtained from L-BTAFM gels from 5 mM to 50 mM. λ_{ex}=258 nm.

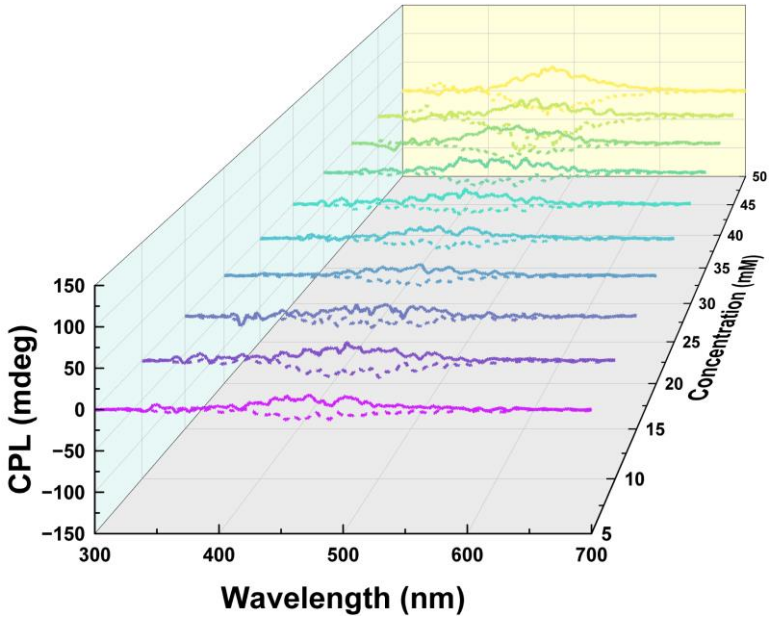

Fig. S15 CPL spectra of the xerogels obtained from L-BTAFM (solid line) and D-BTAFM gels (dashed line) from 5 mM to 50 mM. λ_{ex}=258 nm.

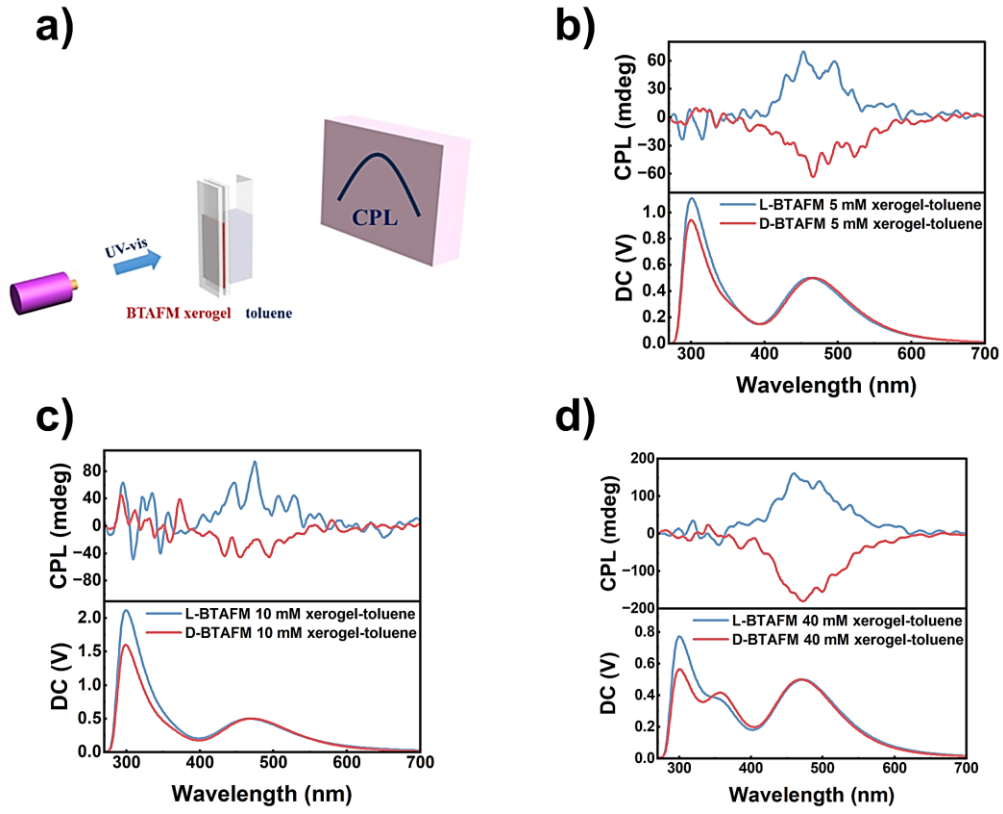

Fig. S16 a) Schematic diagram of the designed CPL testing method showing the relative position between BTECM xerogel and the solvent toluene. The corresponding CPL spectra detected by this testing method using the xerogels obtained from BTECM gels at different concentrations: b) 5 mM, c) 10 mM, and d) 40 mM. λ_{ex}=258 nm.

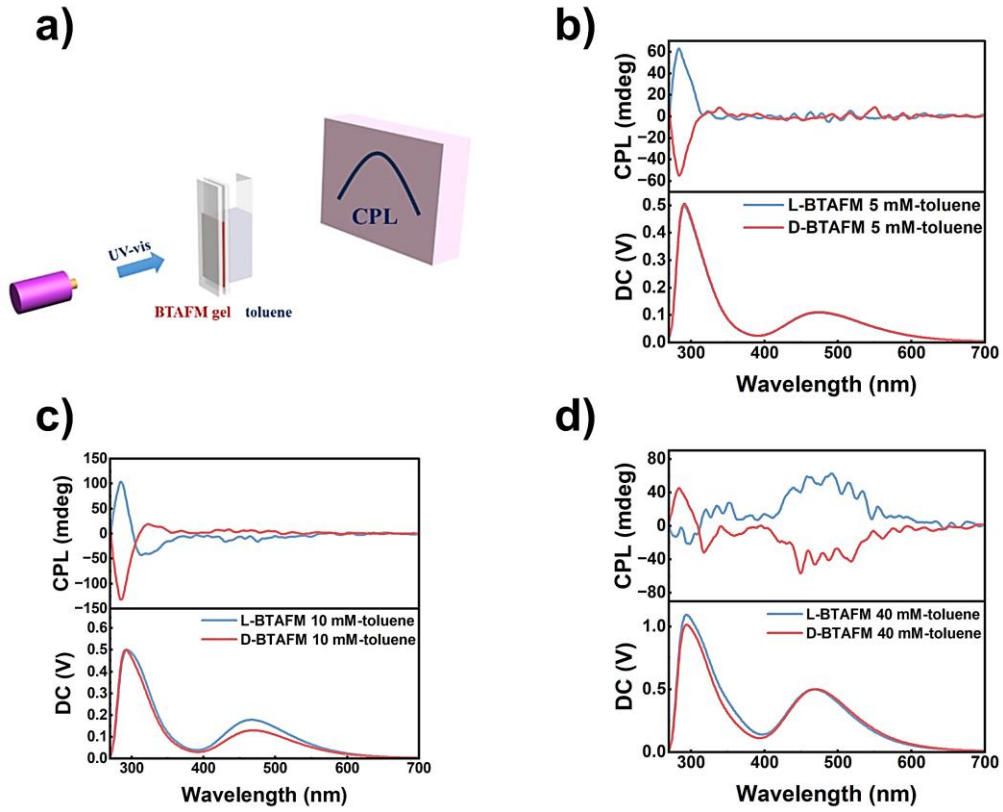

Fig. S17 Schematic diagram of the designed CPL testing method showing the relative position between BTECM gel and the solvent toluene. The corresponding CPL spectra detected by this testing method using BTECM gels at different concentrations: b) 5 mM, c) 10 mM, and d) 40 mM. λ_{ex}=258 nm.

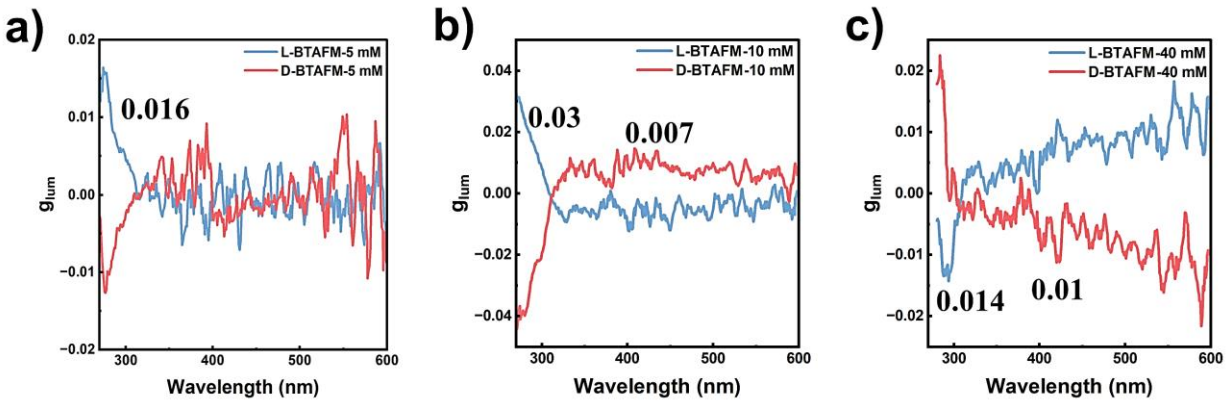

Fig. S18 g_{lum} values of the CPL spectra of BTAFM gels at different concentrations: **a)** 5 mM, **b)** 10 mM, and **c)** 40 mM. λ_{ex}=258 nm.

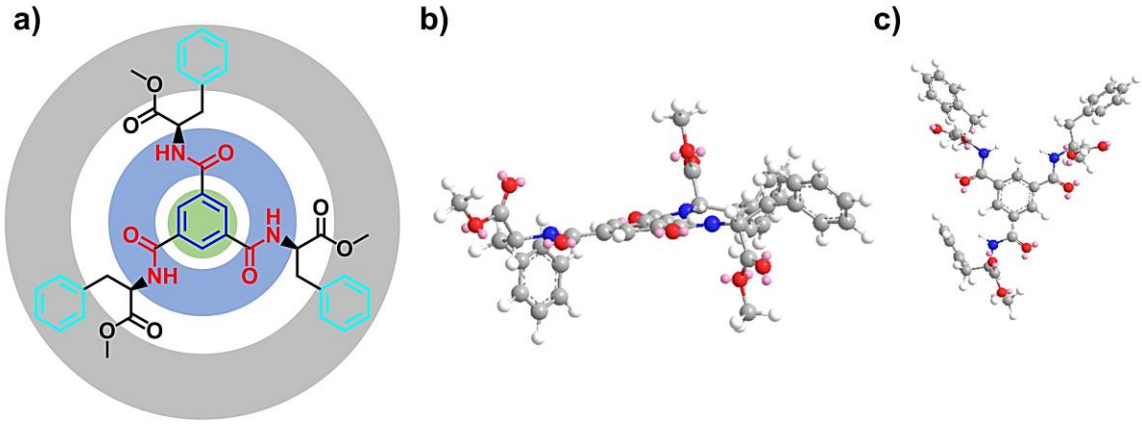

Fig. S19 a) Molecular structure of L-BTAFM. **b)** Main view of L-BTAFM molecule optimized by GaussView. **c)** Left view of L-BTAFM molecule optimized by GaussView. The red, grey, blue and white spheres represent oxygen, carbon, nitrogen and hydrogen atoms, respectively.