Electronic Supplementary Information

Exploring the Role of Molecular Chirality in Photo-Responsiveness of Dipeptide-Based Gels

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Materials and Instruments

Instruments

Hydrogen and carbon nuclear magnetic resonance ($^1$H NMR and $^{13}$C NMR) spectra were recorded on a 500 MHz NMR (Bruker, Germany). Mass spectra (MS) were obtained with a Finnigan LCQ advantage mass spectrometer. All synthesized chiral gelators were purified through Shimadzu LC-20A purity system (Japan) using a chiral chromatographic column (AS-H, 250 mm × 4.6 mm, 5 μm, Daicel Corp., Japan). Optical rotations were recorded on a Perkin-Elmer Model 341 polarimeter. Ultraviolet and visible spectra (UV-Vis) were recorded on a Shimadzu UV-2500 spectrophotometer. Infrared spectra were recorded on a Bruker Vertex 80v Fourier transform infrared (FT-IR) spectrometer in combination with platinum-attenuated total reflection (ATR) cell accessory. Vibrational circular dichroism (VCD) spectra were recorded on a Bruker Vertex 80v Fourier FT-IR spectrometer in combination with a PMA 50 module. Atomic force microscopy (AFM) investigation was conducted on freshly cleaved mica substrates using a Multimode 8 AFM (Bruker, USA) in a tapping mode. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 SEM. Circular dichroism (CD) spectra were obtained with a J-1500 CD spectrometer (JASCO, Japan). X-ray diffraction (XRD) patterns were obtained with a D8 advance X-ray diffractometer (Bruker, USA) using Cu Kα irradiation source ($\lambda=1.54056 \text{ Å}$) at a scan rate of 0.05º s$^{-1}$. A variable power Xe lamp with a 365 nm band-pass filter (Perfect Light Crop., Beijing) is used as the UV light source.

Materials

$\alpha$-L-Asp-L-Phe, $\alpha$-D-Asp-D-Phe, $\alpha$-L-Phe-L-Phe, $\alpha$-D-Phe-D-Phe, $\alpha$-L-Glu-L-Phe, $\alpha$-D-Glu-D-Phe, $\alpha$-L-Asp-L-Trp, $\alpha$-D-Asp-D-Trp, $\alpha$-L-Ala-L-Phe, $\alpha$-D-Ala-D-Phe, Gly-L-Phe, Gly-D-Phe, $\alpha$-L-Asp-L-Asp-L-Phe and $\alpha$-D-Asp-D-Asp-D-Phe (purity: 99%) were purchased from CS-Bio Corp. (Shanghai, P. R. China) and stored at −20 ºC prior to use. L-phenylalanine and D-phenylalanine were purchased from Aladdin Corp. (P. R. China). Triethylamine, deuterated chloroform and deuterated dimethylsulfoxide (DMSO) were purchased from Sigma-Aldrich Corp. (P. R. China).
Chloroform, acetone, methanol, dichloromethane, chloroacetyl chloride, 1,4-dioxane, nitromethane with high purities (99.9%) were purchased from Sinopharm Chemical Reagent Corp. (P. R. China), and chloroform was dried by molecular sieves for 24 hours prior to use.
Synthesis and Characterization

Figure S1. Comparison of $^1$H NMR (a), $^{13}$C NMR (b), MS (c) and IR (d) spectra of L, L-G1 (black curves) and D, D-G1 (red curves) gelators. These spectra clearly indicated that the chemical structures of L, L-G1 and D, D-G1 were identical to each other except their molecular chirality.

**Synthesis and characterization of L-G2**: The same procedure was adopted to prepare gelator L-G2 except the L-Phe-methyl ester was used as reactant (yield: 48%, m.p. 143 $^\circ$C). This compound needed to be further purified through Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm $\times$ 4.6 mm, 5 $\mu$m, Daicel Corp., Japan). $[\alpha]_{20}^D = +120.4^\circ$ (c: 5 mg·mL$^{-1}$, CHCl$_3$). $^1$H NMR (500 MHz, CDCl$_3$): 3.26-3.37 (m, 4H, C-C$_2$H$_2$), 3.82 (s, 6H, OC$_3$H$_3$), 5.12-5.16 (m, 2H, C*H$_2$), 6.70 (d, $J=7.5$ Hz, 2H, CONH$_2$), 7.17 (d, $J=7$ Hz, 4H, Ph-H), 7.27-7.35 (m, 6H, Ph-H), 7.89-7.99 (m, 8H, Ph-H). $^{13}$C NMR (500 MHz, CDCl$_3$): 37.9, 52.5, 53.7, 122.8, 123.2, 127.3, 127.9, 128.1, 128.7, 129.4, 135.8, 136.1, 154.3, 166.0, 172.0. IR: (3291, 1737, 1635, 1578, 1532, 1493, 1435, 1321, 1279, 1215, 1174, 1096 cm$^{-1}$). MS: m/z calcd for C$_{34}$H$_{32}$N$_4$O$_6$: 592.2; found: 593.3. [M+H]$^+$\). Elemental analysis calcd. (%) for C$_{34}$H$_{32}$N$_4$O$_6$: C, 68.91; H, 5.44; N, 9.45. Found: C, 68.88; H, 5.42; N, 9.49.
Synthesis and characterization of D-G2: The same procedure was adopted to prepare gelator D-G2 except the D-Phe-methyl ester was used as reactant (yield: 52%, m.p. 143 °C). This compound needed to be further purified through Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm × 4.6 mm, 5 μm, Daicel Corp., Japan). \([\alpha]_D = -120.3^\circ (c: 5 \text{ mg} \cdot \text{mL}^{-1}, \text{CHCl}_3)\). ¹H NMR (500 MHz, CDCl₃): 3.26-3.37 (m, 4H, C-C₄H₂), 3.81 (s, 6H, OC₃H₃), 5.12-5.16 (m, 2H, C⁺H), 6.72 (d, \(J=7.5\) Hz, 2H, CONH), 7.17 (d, \(J=7\) Hz, 4H, Ph-H), 7.28-7.35 (m, 6H, Ph-H), 7.88-7.98 (m, 8H, Ph-H). ¹³C NMR (500 MHz, CDCl₃): 37.9, 52.5, 53.7, 122.8, 123.2, 127.3, 127.9, 128.1, 128.7, 129.4, 135.8, 136.1, 154.3, 166.0, 172.0. IR: (3291, 1737, 1636, 1577, 1493, 1435, 1321, 1279, 1215, 1174, 1096 cm⁻¹). MS: m/z calcd for C₃₄H₃₂N₄O₆: 592.2; found: 593.2. \([\text{M+H}]^+\). Elemental analysis calcd. (%) for C₃₄H₃₂N₄O₆: C, 68.91; H, 5.44; N, 9.45. Found: C, 68.87; H, 5.45; N, 9.48.

Synthesis and characterization of L, L-G3: The same procedure was adopted to prepare gelator L, L-G3 except the L-Phe-L-Phe-methyl ester was used as reactant (yield: 63%, m.p. 285.6 °C). This compound needed to be further purified through Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm × 4.6 mm, 5 μm, Daicel Corp., Japan). \([\alpha]_D = -124.4^\circ (c: 5 \text{ mg} \cdot \text{mL}^{-1}, \text{DMF})\). ¹H NMR (500 MHz, d₆-DMSO): 2.95-3.13 (m, 8H, C-C₄H₂), 3.60 (s, 6H, OCH₃), 4.52-4.57 (m, 2H, C⁺H), 4.78-4.83 (m, 2H, C⁺H), 7.16-7.22 (m, 4H, Ph-H), 7.24-7.28 (m, 12H, Ph-H), 7.36 (d, \(J=7.5\) Hz, 4H, Ph-H), 7.96-8.01 (m, 8H, Ph-H), 8.57 (d, \(J=7.5\) Hz, 2H, CONH), 8.76 (d, \(J=8.5\) Hz, 2H, CONH). ¹³C NMR (500 MHz, d₆-DMSO): 37.1, 37.4, 46.2, 52.3, 54.2, 55.1, 122.9, 126.7, 127.1, 128.5, 128.7, 129.3, 129.6, 129.7, 137.0, 137.5, 138.7. IR (3285, 1741, 1663, 1632, 1532, 1495, 1436, 1376, 1330, 1279, 1176, 1106 cm⁻¹). MS: m/z calcd for C₅₂H₅₀N₆O₆: 886.4; found: 887.4. \([\text{M+H}]^+\). Elemental analysis calcd. (%) for C₅₂H₅₀N₆O₆: C, 70.41; H, 5.68; N, 9.47. Found: C, 70.39; H, 5.63; N, 9.53.

Synthesis and characterization of D, D-G3: The same procedure was adopted to prepare gelator D, D-G3 except the D-Phe-D-Phe-methyl ester was used as reactant (yield: 67%, m.p. 285.8 °C). This compound needed to be further purified through Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm × 4.6 mm, 5 μm, Daicel Corp., Japan). \([\alpha]_D = -124.4^\circ (c: 5 \text{ mg} \cdot \text{mL}^{-1}, \text{DMF})\).
mm × 4.6 mm, 5 μm, Daicel Corp., Japan). \([\alpha]20 \text{ D} = +124.3^\circ \text{ (c: 5 mg·mL}^{-1}, \text{ DMF).}\)

\(^1\text{H NMR (500 MHz, } d_6\text{-DMSO): 2.97-3.13 \text{ (m, 8H, C-CH}_2\text{), 3.60 (s, 6H, OCH}_3\text{), 4.53-4.56 \text{ (m, 2H, C}*H\text{), 4.78-4.83 (m, 2H, C}*H\text{), 7.16-7.23 (m, 4H, Ph-H), 7.24-7.28 (m, 12H, Ph-H), 7.36 (d, } J=7.5 \text{ Hz, 4H, Ph-H), 7.96-8.02 (m, 8H, Ph-H), 8.59 (d, } J=7.5 \text{ Hz, 2H, CON-H\text{).} \)}

\(^1\text{C NMR (500 MHz, } d_6\text{-DMSO): 37.1, 37.4, 46.0, 52.3, 54.2, 55.1, 122.9, 126.7, 127.1, 128.5, 128.7, 129.3, 129.6, 129.7, 137.0, 137.5, 138.7. IR (3285, 1742, 1663, 1632, 1531, 1494, 1437, 1379, 1329, 1278, 1174, 1108 cm}^{-1}\text{). MS: } m/z \text{ calcd for C}_{52}\text{H}_{50}\text{N}_6\text{O}_8: 886.4; \text{ found: 887.5. } [\text{M+H}]^+.\)

Elemental analysis calcd. (%) for C_{52}H_{50}N_6O_8: C, 70.41; H, 5.68; N, 9.47. Found: C, 70.38; H, 5.64; N, 9.52.

**Synthesis and characterization of L, L-G4:** Same procedure was adopted to prepare gelator L, L-G4 except the L-Glu-L-Phe-methyl ester was used as reactant (yield: 73%, m.p. 225.8 \text{ °C}). This compound needed to be further purified through Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm × 4.6 mm, 5 μm, Daicel Corp., Japan). \([\alpha]20 \text{ D} = +18.6^\circ \text{ (c: 5 mg·mL}^{-1}, \text{ CHCl}_3\text{).} \)

\(^1\text{H NMR (500 MHz, } d_6\text{-DMSO): 1.93-2.09 (m, 4H, C-C}_2\text{), 2.36 (t, } J_1=J_2=8 \text{ Hz, 4H, C-C}_2\text{), 2.97 (m, 4H, C-CH}_2\text{), 3.56 (s, 12H, OCH}_3\text{), 4.50-4.56 (m, 4H, C}*H\text{), 7.18-7.27 (m, 10H, Ph-H), 8.01-8.13 (m, 8H, Ph-H), 8.44 (d, } J=7.5 \text{ Hz, 2H, CON-H\text{).} \)}

\(^1\text{C NMR (500 MHz, } d_6\text{-DMSO): 27.3, 30.5, 37.0, 51.8, 52.3, 53.0, 54.1, 123.0, 127.0, 128.7, 129.5, 129.6, 137.0, 137.5, 137.5, 153.8, 166.1, 171.7, 172.3, 173.3. IR (3290, 1734, 1664, 1635, 1533, 1494, 1436, 1381, 1333, 1296, 1196, 1173, 1106, 1012 cm}^{-1}\text{). MS: } m/z \text{ calcd for C}_{46}\text{H}_{50}\text{N}_6\text{O}_{12}: 878.3; \text{ found: 879.5. } [\text{M+H}]^+.\)

Elemental analysis calcd. (%) for C_{46}H_{50}N_6O_{12}: C, 62.86; H, 5.73; N, 9.56; found: C, 62.80; H, 5.74; N, 9.63.

**Synthesis and characterization of D, D-G4:** The same procedure was adopted to prepare gelator D, D-G4 except the D-Glu-D-Phe-methyl ester was used as reactant (yield: 78%, m.p. 226.0 °C). This compound needed to be further purified through Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm × 4.6 mm, 5 μm, Daicel Corp., Japan). \([\alpha]20 \text{ D} = -18.6^\circ \text{ (c: 5 mg·mL}^{-1}, \text{ CHCl}_3\text{).} \)

\(^1\text{H NMR (500 MHz, } d_6\text{-DMSO): 1.93-2.09 (m, 4H, C-CH}_2\text{), 2.37 (t, } J_1=J_2=8 \text{ Hz, 4H, C-CH}_2\text{), 2.97 (m, 4H, C-CH}_2\text{), 3.56 (s, 12H, OCH}_3\text{), 4.50-4.56 (m, 4H, C}*H\text{), 7.18-7.27 (m, 10H, Ph-H), 8.01-8.13 (m, 8H, Ph-H), 8.44 (d, } J=7.5 \text{ Hz, 2H, CON-H\text{).} \)}

\(^1\text{C NMR (500 MHz, } d_6\text{-DMSO): 27.3, 30.5, 37.0, 51.8, 52.3, 53.0, 54.1, 123.0, 127.0, 128.7, 129.5, 129.6, 137.0, 137.5, 137.5, 153.8, 166.1, 171.7, 172.3, 173.3. IR (3290, 1734, 1664, 1635, 1533, 1494, 1436, 1381, 1333, 1296, 1196, 1173, 1106, 1012 cm}^{-1}\text{). MS: } m/z \text{ calcd for C}_{46}\text{H}_{50}\text{N}_6\text{O}_{12}: 878.3; \text{ found: 879.5. } [\text{M+H}]^+.\)

Elemental analysis calcd. (%) for C_{46}H_{50}N_6O_{12}: C, 62.86; H, 5.73; N, 9.56; found: C, 62.80; H, 5.74; N, 9.63.
C-CH₂), 2.97-3.08 (m, 4H, C-CH₂), 3.57 (s, 12H, OCH₃), 4.49-4.54 (m, 4H, C*H), 7.18-7.27 (m, 10H, Ph-H), 8.01-8.12 (m, 8H, Ph-H), 8.43 (d, J=7.5 Hz, 2H, CONH), 8.64 (d, J=8 Hz, 2H, CONH). ¹³C NMR (500 MHz, d₆-DMSO): 27.3, 30.5, 37.0, 51.8, 52.3, 53.0, 54.1, 123.0, 127.0, 128.7, 129.5, 129.6, 137.0, 137.5, 153.8, 166.1, 171.7, 172.3, 173.3. IR (3290, 1734, 1663, 1635, 1533, 1494, 1436, 1380, 1333, 1296, 1196, 1174, 1106, 1012 cm⁻¹). MS: m/z calcd for C₄₆H₅₀N₆O₁₂: 878.3; found: 879.4. [M+H]⁺. Elemental analysis calcd. (%) for C₄₆H₅₀N₆O₁₂: C, 62.86; H, 5.73; N, 9.56; found: C, 62.81; H, 5.74; N, 9.62.

**Synthesis and characterization of L, L-G5:** Same procedure was adopted to prepare gelator L, L-G5 except the L-Asp-L-Trp-methyl ester was used as reactant (yield: 65%, m.p. 143.0 °C). This compound needed to be further purified through Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm × 4.6 mm, 5 μm, Daicel Corp., Japan). [α]20 D = +36.6° (c: 5 mg·mL⁻¹, CH₃OH). ¹H NMR (500 MHz, d₆-DMSO): 2.76-2.92 (m, 4H, C-CH₂), 3.12-3.22 (m, 4H, C-CH₂), 3.60 (d, J=10.5 Hz, 12H, OCH₃), 4.54-4.59 (m, 2H, C*H), 4.93-4.98 (m, 2H, C*H), 6.96 (t, J₁=J₂=7.5 Hz, 2H, Ph-H), 7.05 (t, J₁=J₂=7.5 Hz, 2H, Ph-H), 7.19 (s, 2H, Ph-H), 7.34 (d, J=8 Hz, 2H, Ph-H) 7.49 (d, J=7.5 Hz, 2H, Ph-H), 8.02- 8.08 (m, 8H, Ph-H), 8.29 (d, J=7.5 Hz, 2H, CONH), 8.81 (d, J=8 Hz, 2H, CONH), 10.85 (s, 2H, Ph-NH). ¹³C NMR (500 MHz, d₆-DMSO): 27.3, 36.1, 50.5, 52.0, 52.3, 53.8, 109.7, 111.9, 118.4, 118.9, 121.4, 123.0, 124.2, 127.6, 129.4, 136.6, 137.0, 153.9, 166.1, 170.9, 171.1, 172.5. IR (3300, 1737, 1632, 1529, 1437, 1341, 1282, 1251, 1202, 1093, 1074, 1010 cm⁻¹). MS: m/z calcd for C₄₈H₄₈N₈O₁₂: 928.3; found: 929.4. [M+H]⁺. Elemental analysis calcd. (%) for C₄₈H₄₈N₈O₁₂: C, 62.06; H, 5.21; N, 12.06; found: C, 62.03; H, 5.17; N, 12.12.

**Synthesis and characterization of D, D-G5:** The same procedure was adopted to prepare gelator D, D-G5 except the D-Asp-D-Trp-methyl ester was used as reactant (yield: 71%, m.p. 142.8 °C). This compound needed to be further purified through Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm × 4.6 mm, 5 μm, Daicel Corp., Japan). [α]20 D = −36.7° (c: 5 mg·mL⁻¹, CH₃OH). ¹H NMR (500 MHz, d₆-DMSO): 2.68-2.79 (m, 4H, C-CH₂), 3.08-3.22 (m, 4H, C-CH₂), 3.59 (d, J=10 Hz, 12H, OCH₃), 4.55-4.59 (m, 2H, C*H), 4.91-4.95 (m, 2H, C*H), 6.95
(t, \(J_1=J_2=7.5\) Hz, 2H, Ph-\(H\)), 7.05 (t, \(J_1=J_2=7.5\) Hz, 2H, Ph-\(H\)), 7.15 (s, 2H, Ph-\(H\)), 7.34 (d, \(J=8\) Hz, 2H, Ph-\(H\)) 7.49 (d, \(J=8\) Hz, 2H, Ph-\(H\)), 8.01-8.08 (m, 8H, Ph-\(H\)), 8.34 (d, \(J=8\) Hz, 2H, CON\(H\)), 8.82 (d, \(J=8\) Hz, 2H, CON\(H\)), 10.89 (s, 2H, Ph-N\(H\)). \(^{13}\)C NMR (500 MHz, \(d_6\)-DMSO): 27.5, 36.1, 50.4, 52.0, 52.4, 53.6, 109.7, 111.9, 118.4, 118.9, 121.4, 123.0, 124.2, 127.5, 129.4, 136.6, 137.0, 153.9, 166.1, 170.7, 171.1, 172.5. IR (3299, 1737, 1631, 1529, 1437, 1340, 1282, 1251, 1202, 1092, 1074, 1010 cm\(^{-1}\)). MS: m/z calcd for C\(_{48}\)H\(_{48}\)N\(_8\)O\(_{12}\): 928.3; found: 929.4. [M+H]\(^+\). Elemental analysis calcd. (%) for C\(_{48}\)H\(_{48}\)N\(_8\)O\(_{12}\): C, 62.06; H, 5.21; N, 12.06; found: C, 62.03; H, 5.20; N, 12.10.

**Synthesis and characterization of L, L-G6:** The same procedure was adopted to prepare gelator L, L-G6 except the L-Ala-L-Phe-methyl ester was used as reactant (yield: 56%, m.p. 241.2 °C). This compound needed to be further purified through Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm \(\times\) 4.6 mm, 5 \(\mu\)m, Daicel Corp., Japan). \([\alpha]_{20}^D = -73.5^\circ\) (c: 4 mg·mL\(^{-1}\), DMF). \(^1\)H NMR (500 MHz, \(d_6\)-DMSO): 1.35 (d, \(J=7\) Hz, 6H, C-\(CH_3\)), 3.00-3.18 (m, 4H, C-\(CH_2\)), 3.64 (s, 6H, OCH\(_3\)), 4.32-4.38 (m, 2H, C*\(H\)), 4.77-4.82 (m, 2H, C\(^*\)\(H\)), 7.16-7.30 (m, 10H, Ph-\(H\)), 7.94-8.02 (m, 8H, Ph-\(H\)), 8.63 (d, \(J=7\) Hz, 2H, CON\(H\)), 8.79 (d, \(J=8.5\) Hz, 2H, CON\(H\)). \(^{13}\)C NMR (500 MHz, \(d_6\)-DMSO): 17.4, 48.2, 52.3, 55.1, 122.9, 126.7, 128.6, 128.7, 129.3, 129.6, 137.0, 138.8, 153.8, 165.9, 171.9, 173.5. IR (3281, 1740, 1660, 1632, 1531, 1437, 1378, 1281, 1212, 1150, 1054, 1012 cm\(^{-1}\)). MS: m/z calcd for C\(_{40}\)H\(_{42}\)N\(_6\)O\(_8\): 734.3; found: 735.3. [M+H]\(^+\). Elemental analysis calcd. (%) for C\(_{40}\)H\(_{42}\)N\(_6\)O\(_8\): C, 65.38; H, 5.76; N, 11.44; found: C, 65.40; H, 5.73; N, 11.47.

**Synthesis and characterization of D, D-G6:** The same procedure was adopted to prepare gelator D, D-G6 except the D-Ala-D-Phe-methyl ester was used as reactant (yield: 51%, m.p. 240.8 °C). This compound needed to be further purified through Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm \(\times\) 4.6 mm, 5 \(\mu\)m, Daicel Corp., Japan). \([\alpha]_{20}^D = +73.4^\circ\) (c: 4 mg·mL\(^{-1}\), DMF). \(^1\)H NMR (500 MHz, \(d_6\)-DMSO): 1.35 (d, \(J=7\) Hz, 6H, C-\(CH_3\)), 2.99-3.17 (m, 4H, C-\(CH_2\)), 3.65 (s, 6H, OCH\(_3\)), 4.32-4.38 (m, 2H, C\(^*\)\(H\)), 4.77-4.82 (m, 2H, C\(^*\)\(H\)), 7.16-7.30 (m, 10H, Ph-\(H\)), 7.94-8.02 (m, 8H, Ph-\(H\)), 8.63 (d, \(J=7\) Hz, 2H, CON\(H\)), 8.78 (d, \(J=8.5\) Hz, 2H, CON\(H\)). \(^{13}\)C NMR (500 MHz, \(d_6\)-DMSO): 17.4, 48.3, 52.3, 55.1, 122.9, 126.7, 128.6, 128.7, 129.3, 129.6, 137.0, 138.8, 153.8, 165.9, 171.9, 173.5. IR (3281, 1740, 1660, 1632, 1531, 1437, 1378, 1281, 1212, 1150, 1054, 1012 cm\(^{-1}\)). MS: m/z calcd for C\(_{40}\)H\(_{42}\)N\(_6\)O\(_8\): 734.3; found: 735.3. [M+H]\(^+\). Elemental analysis calcd. (%) for C\(_{40}\)H\(_{42}\)N\(_6\)O\(_8\): C, 65.38; H, 5.76; N, 11.44; found: C, 65.40; H, 5.73; N, 11.47.
128.6, 128.7, 129.2, 129.5, 137.1, 138.8, 153.8, 165.9, 171.8, 173.4. IR (3281, 1740, 1660, 1632, 1531, 1437, 1378, 1281, 1212, 1150, 1054, 1012 cm⁻¹). MS: m/z calcd for C₄₀H₄₂N₆O₈: 734.3; found: 735.3. [M+H]+. Elemental analysis calcd. (%) for C₄₀H₄₂N₆O₈: C, 64.38; H, 5.76; N, 11.44; found: C, 64.33; H, 5.76; N, 11.48.

**Synthesis and characterization of L-G7**: The same procedure was adopted to prepare gelator L-G7 except the Gly-L-Phe-methyl ester was used as reactant (yield: 41%, m.p. 216.8 °C). This compound needed to be further purified through Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm × 4.6 mm, 5 μm, Daicel Corp., Japan). [α]D = +7.0º (c: 3 mg·mL⁻¹, DMF). ¹H NMR (500 MHz, d₆-DMSO): 2.93-3.07 (m, 4H, C-C₄H₂), 3.62 (s, 6H, OCH₃), 3.87-3.98 (m, 4H, C-C₄H₂), 4.50-4.54 (m, 2H, C*H), 7.20-7.29 (m, 10H, Ph-H), 8.01-8.11 (m, 8H, Ph-H), 8.42 (d, J=7 Hz, 2H, CONH), 8.89 (t, J₁=J₂=6 Hz, 2H, CONH). ¹³C NMR (500 MHz, d₆-DMSO): 37.2, 42.6, 52.4, 54.1, 123.0, 127.1, 128.8, 129.2, 129.6, 137.0, 137.5, 153.8, 166.1, 169.4, 172.6. IR (3293, 1751, 1689, 1644, 1519, 1485, 1436, 1376, 1312, 1270, 1215, 1131, 1106, 1080, 1055, 1034, 1011 cm⁻¹). MS: m/z calcd for C₃₈H₃₈N₆O₈: 706.3; found: 707.3. [M+H]+. Elemental analysis calcd. (%) for C₃₈H₃₈N₆O₈: C, 64.58; H, 5.42; N, 11.89; found: C, 64.53; H, 5.41; N, 11.95.

**Synthesis and characterization of D-G7**: The same procedure was adopted to prepare gelator D-G7 except the Gly-D-Phe-methyl ester was used as reactant (yield: 43%, m.p. 216.4 ºC). This compound needed to be further purified through Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm × 4.6 mm, 5 μm, Daicel Corp., Japan). [α]D = −7.0º (c: 3 mg·mL⁻¹, DMF). ¹H NMR (500 MHz, d₆-DMSO): 2.93-3.07 (m, 4H, C-C₄H₂), 3.62 (s, 6H, OCH₃), 3.88-3.98 (m, 4H, C-C₄H₂), 4.50-4.54 (m, 2H, C*H), 7.20-7.29 (m, 10H, Ph-H), 8.01-8.11 (m, 8H, Ph-H), 8.42 (d, J=7.5 Hz, 2H, CONH), 8.89 (t, J₁=J₂=6 Hz, 2H, CONH). ¹³C NMR (500 MHz, d₆-DMSO): 37.3, 42.7, 52.4, 54.1, 123.0, 127.1, 128.8, 129.2, 129.6, 137.0, 137.5, 153.8, 166.1, 169.4, 172.4. IR (3292, 1751, 1690, 1644, 1519, 1485, 1435, 1376, 1312, 1270, 1215, 1131, 1106, 1080, 1055, 1034, 1011 cm⁻¹). MS: m/z calcd for C₃₈H₃₈N₆O₈: 706.3; found: 707.3. [M+H]+. Elemental analysis calcd. (%) for C₃₈H₃₈N₆O₈: C, 64.58; H, 5.42; N, 11.89; found: C, 64.56; H, 5.43; N, 11.92.
Synthesis and characterization of L, L, L-G8: The same procedure was adopted to prepare gelator L, L, L-G8 except the L-Asp-L-Asp-L-Phe-methyl ester was used as reactant (yield: 73%, m.p. 165.5 °C). This compound needed to be further purified through Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm × 4.6 mm, 5 μm, Daicel Corp., Japan). \([\alpha]_{20}D = +104.0^\circ\) (c: 5 mg·mL\(^{-1}\), CHCl\(_3\)). \(^1H\) NMR (500 MHz, \(d_6\)-DMSO): 2.56-2.61 (m, 2H, C-CH\(_2\)), 2.71-2.82 (m, 4H, C-CH\(_3\)), 2.88-3.06 (m, 6H, C-CH\(_2\)), 3.54 (s, 6H, OCH\(_3\)), 3.59 (s, 6H, OCH\(_3\)), 3.62 (s, 6H, OCH\(_3\)), 4.45-4.49 (m, 2H, C*H), 4.62-4.67 (m, 2H, C*H), 4.84-4.88 (m, 2H, C*H), 7.20-7.29 (m, 10H, Ph-H), 8.01-8.11 (m, 8H, Ph-H), 8.17 (d, \(J=7.5\) Hz, 2H, CONH), 8.30 (d, \(J=8.5\) Hz, 2H, CONH), 8.91 (d, \(J=7.5\) Hz, 2H, CONH). \(^13C\) NMR (500 MHz, \(d_6\)-DMSO): 35.9, 36.2, 37.0, 49.9, 50.7, 51.9, 52.0, 52.3, 54.2, 123.0, 127.0, 128.7, 129.4, 129.5, 136.8, 137.4, 153.9, 166.3, 170.6, 170.8, 170.9, 171.3, 172.0. IR (3289, 3064, 2952, 1724, 1649, 1529, 1436, 1366, 1285, 1211, 1172, 1054 cm\(^{-1}\)). MS: m/z calcd for C\(_{54}\)H\(_{60}\)N\(_8\)O\(_{18}\): 1108.4; found: 1109.4. [M+H]\(^+\). Elemental analysis calcd. (%) for C\(_{54}\)H\(_{60}\)N\(_8\)O\(_{18}\): C, 58.48; H, 5.45; N, 10.10; found: C, 58.46; H, 5.47; N, 10.13.

Synthesis and characterization of D, D, D-G8: The same procedure was adopted to prepare gelator D, D, D-G8 except the D-Asp-D-Asp-D-Phe-methyl ester was used as reactant (yield: 77%, m.p. 165.8 °C). This compound needed to be further purified through Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm × 4.6 mm, 5 μm, Daicel Corp., Japan). \([\alpha]_{20}D = -103.9^\circ\) (c: 5 mg·mL\(^{-1}\), CHCl\(_3\)). \(^1H\) NMR (500 MHz, \(d_6\)-DMSO): 2.56-2.61 (m, 2H, C-CH\(_2\)), 2.71-2.82 (m, 4H, C-CH\(_3\)), 2.88-3.06 (m, 6H, C-CH\(_2\)), 3.54 (s, 6H, OCH\(_3\)), 3.59 (s, 6H, OCH\(_3\)), 3.62 (s, 6H, OCH\(_3\)), 4.45-4.49 (m, 2H, C*H), 4.62-4.67 (m, 2H, C*H), 4.84-4.88 (m, 2H, C*H), 7.20-7.29 (m, 10H, Ph-H), 8.01-8.11 (m, 8H, Ph-H), 8.17 (d, \(J=8\) Hz, 2H, CONH), 8.30 (d, \(J=8\) Hz, 2H, CONH), 8.91 (d, \(J=7.5\) Hz, 2H, CONH). \(^13C\) NMR (500 MHz, \(d_6\)-DMSO): 35.9, 36.2, 37.0, 49.9, 50.7, 51.9, 52.0, 52.3, 54.2, 123.0, 127.0, 128.7, 129.4, 129.5, 136.8, 137.4, 153.9, 166.3, 170.6, 170.8, 170.9, 171.3, 172.0. IR (3289, 3064, 2952, 1724, 1649, 1529, 1436, 1366, 1285, 1211, 1172, 1054 cm\(^{-1}\)). MS: m/z calcd for C\(_{54}\)H\(_{60}\)N\(_8\)O\(_{18}\): 1108.4; found: 1109.4. [M+H]\(^+\). Elemental analysis calcd. (%) for C\(_{54}\)H\(_{60}\)N\(_8\)O\(_{18}\): C, 58.48; H, 5.45; N, 10.10; found: C, 58.46; H, 5.47; N, 10.13.
analysis calcd. (%) for C$_{54}$H$_{60}$N$_8$O$_{18}$: C, 58.48; H, 5.45; N, 10.10; found: C, 58.43; H, 5.44; N, 10.15.
Supplementary Figures

Figure S2. Self-assembled morphologies of L, L-G1 (a, c, e, g) and D, D-G1 (b, d, f, h) in chloroform on freshly cleaved mica surface. (a, b) 0.05 mg·mL$^{-1}$; (c, d) 0.1 mg·mL$^{-1}$; (e, f) 0.3 mg·mL$^{-1}$; (g, h) 0.5 mg·mL$^{-1}$, observed by AFM in a tapping mode. According to (a, b), molecular self-assembly would not happen at the concentration of 0.05 mg·mL$^{-1}$. With the increase of gelator concentrations (i.e. 0.1, 0.3 and 0.5 mg·mL$^{-1}$), L, L-G1 or D, D-G1 gradually self-assembled into a large number of nanofibers with uniform length and height, the nanopatterns only differed in their packing densities of fibers. Scan bars: 2 μm.
Figure S3. The apparatus used in the UV light irradiation experiment. The gel temperature was kept at 25 °C by a temperature control plate. A variable power Xe lamp with a 365 nm band-pass filter (Perfect Light Crop., Beijing) was used as the UV light source.
Figure S4. UV-Vis spectra of L, L-G1 and D, D-G1 in chloroform irradiated by UV light (λ: 365 nm, intensity: 5 mW·cm⁻²) at different time intervals, the concentrations of solutions were 0.05 mg·mL⁻¹, obtained by Shimadzu UV-2500 spectrophotometer at 25 °C. Identical absorption intensity changes of L, L-G1 and D, D-G1 spectra in response to UV light irradiation indicated that this pair of gelators had the same speed of trans- to cis- (E/Z)-isomerization.
Figure S5. CD spectra (a) of L, L-G1 and D, D-G1 in chloroform/ methanol (v/v: 1/3, 0.05 mg·mL$^{-1}$), and UV-Vis (b) spectra of L, L-G1 and D, D-G1 in chloroform/ methanol (v/v: 1/3, 0.05 mg·mL$^{-1}$) before and after 15 min UV light ($\lambda$: 365 nm, intensity: 5 mW·cm$^{-2}$) irradiation. Black curves refer to L, L-G1; red ones refer to D, D-G1. The CD and UV spectra indicated the identical E/Z-isomerization speeds and the mirror-symmetric conformations of L, L-G1 and D, D-G1 in chloroform/methanol (v/v: 1:3). These data further revealed that L, L-G1 and D, D-G1 possessed nearly symmetric stereo-conformation at molecular level.
Figure S6. Self-assembled morphologies of L, L- (a, c) and D, D- (b, d) G1 gels before (a, b) and after (c, d) 30 min UV light irradiation (λ: 365 nm, intensity: 5 mW·cm⁻²), observed by SEM on a larger scale. Gel formation condition: chloroform/methanol (v/v: 1/3, 5.0 mg·mL⁻¹). These data clearly indicated that significant chiral discrimination could also be observed on a large scale.
Figure S7. Self-assembled morphologies of L, L-G1 and D, D-G1 observed by AFM on a large scale. Self-assembled morphologies and section profiles along the green lines of L, L-G1 (a, c) and D, D-G1 (b, d) in chloroform (0.5 mg·mL$^{-1}$) before (a, b) and after (c, d) 15 min UV light irradiation ($\lambda$: 365 nm, intensity: 5 mW·cm$^{-2}$), as observed by AFM in a large scale (Scale bars: 4 μm for (a-c) and 8 μm for (d)). These data indicated that significant chiral discrimination could also be observed on a large scale.
Figure S8. Photographs of L, L-G3 and D, D-G3 gels exposed to UV light irradiation at different time. Gel-sol transition of L, L-G3 and D, D-G3 gels (solvent: 1, 4-dioxane, concentration: 5 mg·mL$^{-1}$) upon UV light irradiation treatment. After 30 min, 60 min and 120 min of UV light irradiation ($\lambda$: 365 nm, intensity: 5 mW·cm$^{-2}$), L, L-G3 and D, D-G3 still maintained gel status, which revealed the strong gelation capacities of L, L-G3 or D, D-G3 attributed to intensive $\pi$–$\pi$ stacking among Phe-Phe units. Under this condition, the gelation force of L, L-G3 or D, D-G3 was far superior to the E/Z-isomerization force driven by UV light and the chiral discrimination between L, L- and D. D-G3 gels could not be detected during the E/Z-isomerization process.
Figure S9. Optimized structures of trans- and cis-isomers of D, D-G1, obtained by density functional theory (DFT) calculations at the 6-311G level (Gaussian), using chloroform as a solvent parameter. Intramolecular H-bonds with different lengths are displayed by green dotted lines.
Figure S10. Circular dichroism (CD) spectra of gelators G2—G8. CD spectra of (a) L-G2 and D-G2 (CH$_2$Cl$_2$, 0.06 mg·mL$^{-1}$), (b) L-G3 and D, D-G3 (DMSO, 0.10 mg·mL$^{-1}$), (c) L, L-G4 and D, D-G4 (CHCl$_3$, 0.10 mg·mL$^{-1}$), (d) L, L-G5 and D, D-G5 (CH$_2$Cl$_2$, 0.04 mg·mL$^{-1}$), (e) L, L-G6 and D, D-G6 (CH$_2$Cl$_2$, 0.06 mg·mL$^{-1}$), (f) L-G7 and D-G7 (CH$_3$OH, 0.06 mg·mL$^{-1}$), (g) L, L, L-G8 and D, D, D-G8 (CHCl$_3$, 0.10 mg·mL$^{-1}$) at 25 ºC. Black curves refer to L-gelators, red curves refer to D-gelators.
Supplementary Table

Gelation abilities of G1-G8 were tested in various solvents at room temperature by a typical heating-cooling procedure. The results are shown in Supplementary Table 1 (G=gel; P=precipitate; S=soluble; I=insoluble), and the minimum gelation concentrations are also presented (mg·mL⁻¹).

Table S1. Gelation abilities of G1-G8 in various organic solvents or mixed solvents.

<table>
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<th>Solvent</th>
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<th>G3</th>
<th>G4</th>
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<th>G7</th>
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<tr>
<td>CHCl₃/CH₃OH (1/3, v/v)</td>
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<td>S</td>
<td>I</td>
<td>G</td>
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