Electronic Supplementary Information

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

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Contents

Materials and Instruments

Instruments

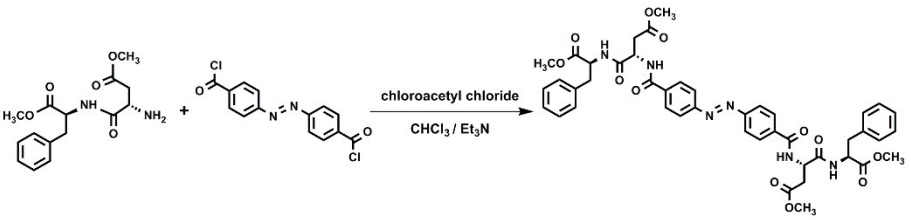
Hydrogen and carbon nuclear magnetic resonance (^{1}H NMR1 and ^{13}C NMR) spectra were rec2orded on a 500 MHz NMR (Bruker, Germany). Mass spectra (MS) were obtained with a Finnigan LCQ advantage mass spectrometer. All synthesized chiral gelators were purified through Shimadzu LC-20A purity system (Japan) 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 (λ=1.54056 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

α-L-Asp-L-Phe, α-D-Asp-D-Phe, α-L-Phe-L-Phe, α-D-Phe-D-Phe, α-L-Glu-L-Phe, α-D-Glu-D-Phe, α-L-Asp-L-Trp, α-D-Asp-D-Trp, α-L-Ala-L-Phe, α-D-Ala-D-Phe, Gly-L-Phe, Gly-D-Phe, α-L-Asp-L-Asp-L-Phe and α-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).

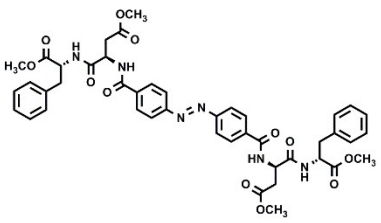
Chloroform, acetone, methanol, dichloromethane, chloroacetyl chloride, 1,4-dioxane, nitromethane with high purities (99.9%) were purchased from Sinopharm Chemical Reagent Corp. (P. R. China), and chloroform was dried by molecular sieves for 24 hours prior to use.

Synthesis and Characterization

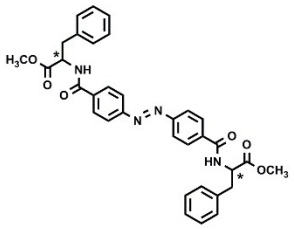


α-L-Asp-L-Phe

L, L-G1



D, D-G1



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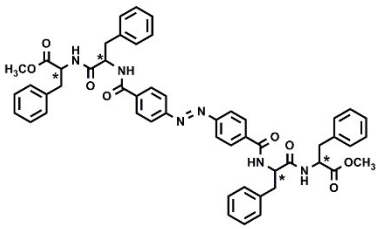

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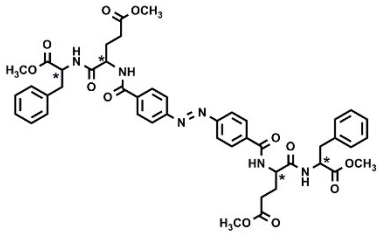

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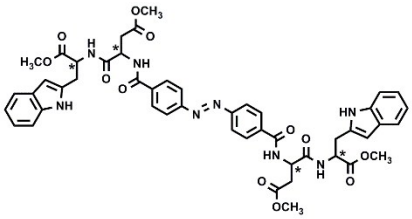

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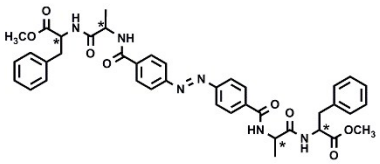

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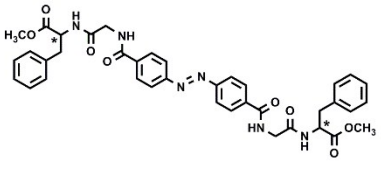

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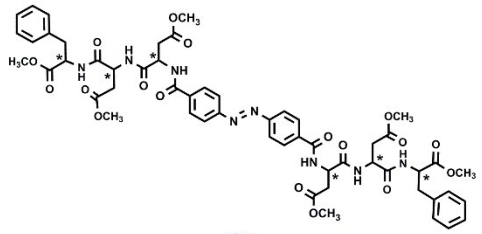

G8

Scheme S1. Chemical structures of G1–G8. Synthetic method of L, L-**G1** (upper part). Chemical structures of D, D-**G1** and other seven pairs of reference gelators (**G2**–**G8**) with different di-, tri-peptide or amino acid arms (lower part).

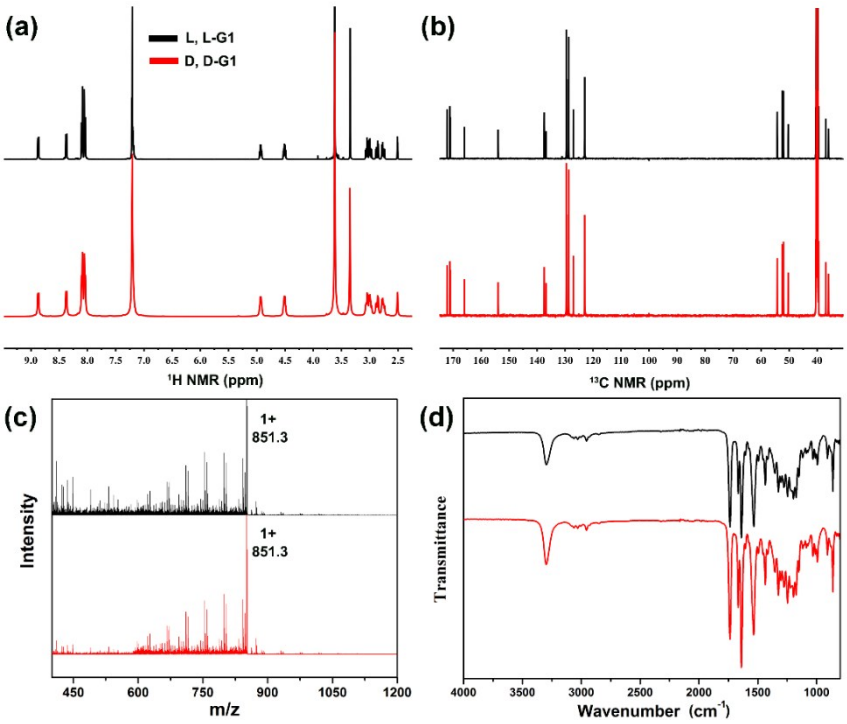

Figure S1. Comparison of ^{1}H NMR (a), ^{13}C NMR (b), MS (c) and IR (d) spectra of L, L-G1 (black curves) and D, D-G1 (red curves) gelators. These spectra clearly indicated that the chemical structures of L, L-**G1** and D, D-**G1** were identical to each other except their molecular chirality.

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 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]20 D = +120.4º (c: 5 mg·mL^{-1}, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 3.26-3.37 (m, 4H, C-CH_2), 3.82 (s, 6H, OCH_3), 5.12-5.16 (m, 2H, C*H), 6.70 (d, J=7.5 Hz, 2H, CONH), 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 $C_{34}H_{32}N_4O_6$: 592.2; found: 593.3. $[M+H]^+$. Elemental analysis calcd. (%) for $C_{34}H_{32}N_4O_6$: 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 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]20 D = –120.3º (c: 5 mg·mL^{-1}, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 3.26-3.37 (m, 4H, C-C*H*$_2$), 3.81 (s, 6H, OC*H*$_3$), 5.12-5.16 (m, 2H, C**H*), 6.72 (d, *J*=7.5 Hz, 2H, CON*H*), 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*). ^{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, 1636, 1577, 1531, 1493, 1435, 1321, 1279, 1215, 1174, 1096 cm^{-1}). MS: m/z calcd for $C_{34}H_{32}N_4O_6$: 592.2; found: 593.2. $[M+H]^+$. Elemental analysis calcd. (%) for $C_{34}H_{32}N_4O_6$: 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 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]20 D = –124.4º (c: 5 mg·mL^{-1}, DMF). ^{1}H NMR (500 MHz, d_6-DMSO): 2.95-3.13 (m, 8H, C-C*H*$_2$), 3.60 (s, 6H, OC*H*$_3$), 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, CON*H*), 8.76 (d, *J*=8.5 Hz, 2H, CON*H*). ^{13}C NMR (500 MHz, d_6-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 $C_{52}H_{50}N_6O_8$: 886.4; found: 887.4. $[M+H]^+$. Elemental analysis calcd. (%) for $C_{52}H_{50}N_6O_8$: C, 70.41; H, 5.68; N, 9.47. Found: C, 70.39; 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 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]20 D = +124.3º (c: 5 mg·mL^{-1}, DMF). ^{1}H NMR (500 MHz, d_6-DMSO): 2.97-3.13 (m, 8H, C-CH_2), 3.60 (s, 6H, OCH_3), 4.53-4.56 (m, 2H, C*H), 4.78-4.83 (m, 2H, C*H), 7.16-7.23 (m, 4H, Ph-H), 7.24-7.28 (m, 12H, Ph-H), 7.36 (d, J=7.5 Hz, 4H, Ph-H), 7.96-8.02 (m, 8H, Ph-H), 8.59 (d, J=7.5 Hz, 2H, CONH), 8.78 (d, J=8.5 Hz, 2H, CONH). ^{13}C NMR (500 MHz, d_6-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}). MS: m/z calcd for $C_{52}H_{50}N_6O_8$: 886.4; found: 887.5. $[M+H]^+$. 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 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]20 D = +18.6º (c: 5 mg·mL^{-1}, $CHCl_3$). ^{1}H NMR (500 MHz, d_6-DMSO): 1.93-2.09 (m, 4H, C-CH_2), 2.36 (t, J_1=J_2=8 Hz, 4H, C-CH_2), 2.97 (m, 4H, C-CH_2), 3.56 (s, 12H, OCH_3), 4.50-4.56 (m, 4H, C*H), 7.18-7.27 (m, 10H, Ph-H), 8.01-8.13 (m, 8H, Ph-H), 8.44 (d, J=7.5 Hz, 2H, CONH), 8.64 (d, J=7.5 Hz, 2H, CONH). ^{13}C NMR (500 MHz, d_6-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, 1664, 1635, 1533, 1494, 1436, 1381, 1333, 1296, 1196, 1173, 1106, 1012 cm^{-1}). MS: m/z calcd for $C_{46}H_{50}N_6O_{12}$: 878.3; found: 879.5. $[M+H]^+$. 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 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]20 D = –18.6º (c: 5 mg·mL^{-1}, $CHCl_3$). ^{1}H NMR (500 MHz, d_6-DMSO): 1.93-2.09 (m, 4H, C-CH_2), 2.37 (t, J_1=J_2=8 Hz, 4H,

C-CH_2), 2.97-3.08 (m, 4H, C-CH_2), 3.57 (s, 12H, OCH_3), 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). ^{13}C NMR (500 MHz, d_6-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 $C_{46}H_{50}N_6O_{12}$: 878.3; found: 879.4. $[M+H]^+$. Elemental analysis calcd. (%) for $C_{46}H_{50}N_6O_{12}$: C, 62.86; H, 5.73; N, 9.56; found: C, 62.81; 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 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]20 D = +36.6º (c: 5 mg·mL^{-1}, CH_3OH). ^{1}H NMR (500 MHz, d_6-DMSO): 2.76-2.92 (m, 4H, C-CH_2), 3.12-3.22 (m, 4H, C-CH_2), 3.60 (d, J=10.5 Hz, 12H, OCH_3), 4.54-4.59 (m, 2H, C*H), 4.93-4.98 (m, 2H, C*H), 6.96 (t, J_1=J_2=7.5 Hz, 2H, Ph-H), 7.05 (t, J_1=J_2=7.5 Hz, 2H, Ph-H), 7.19 (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). ^{13}C NMR (500 MHz, d_6-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 $C_{48}H_{48}N_8O_{12}$: 928.3; found: 929.4. $[M+H]^+$. Elemental analysis calcd. (%) for $C_{48}H_{48}N_8O_{12}$: 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 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]20 D = –36.7º (c: 5 mg·mL^{-1}, CH_3OH). ^{1}H NMR (500 MHz, d_6-DMSO): 2.68-2.79 (m, 4H, C-CH_2), 3.08-3.22 (m, 4H, C-CH_2), 3.59 (d, J=10 Hz, 12H, OCH_3), 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 $C_{48}H_{48}N_8O_{12}$: 928.3; found: 929.4. $[M+H]^+$. Elemental analysis calcd. (%) for $C_{48}H_{48}N_8O_{12}$: 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 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]20 D = –73.5º (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 $C_{40}H_{42}N_6O_8$: 734.3; found: 735.3. $[M+H]^+$. Elemental analysis calcd. (%) for $C_{40}H_{42}N_6O_8$: 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 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]20 D = +73.4º (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*), 7,93-8.01 (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, 123.0, 126.7,

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 $C_{40}H_{42}N_6O_8$: 734.3; found: 735.3. $[M+H]^+$. Elemental analysis calcd. (%) for $C_{40}H_{42}N_6O_8$: 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 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]20 D = +7.0º (c: 3 mg·mL^{-1}, DMF). ^{1}H NMR (500 MHz, d_6-DMSO): 2.93-3.07 (m, 4H, C-CH_2), 3.62 (s, 6H, OCH_3), 3.87-3.98 (m, 4H, C-CH_2), 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, J_1=J_2=6 Hz, 2H, CONH). ^{13}C NMR (500 MHz, d_6-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 $C_{38}H_{38}N_6O_8$: 706.3; found: 707.3. $[M+H]^+$. Elemental analysis calcd. (%) for $C_{38}H_{38}N_6O_8$: 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]20 D = –7.0º (c: 3 mg·mL^{-1}, DMF). ^{1}H NMR (500 MHz, d_6-DMSO): 2.93-3.07 (m, 4H, C-CH_2), 3.62 (s, 6H, OCH_3), 3.88-3.98 (m, 4H, C-CH_2), 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, J_1=J_2=6 Hz, 2H, CONH). ^{13}C NMR (500 MHz, d_6-DMSO): 37.2, 42.7, 52.4, 54.1, 123.0, 127.2, 128.8, 129.2, 129.6, 137.0, 137.5, 153.8, 166.1, 169.4, 172.4. IR (3293, 1751, 1689, 1644, 1519, 1485, 1436, 1376, 1311, 1270, 1214, 1131, 1106, 1080, 1055, 1033, 1010 cm^{-1}). MS: m/z calcd for $C_{38}H_{38}N_6O_8$: 706.3; found: 707.2. $[M+H]^+$. Elemental analysis calcd. (%) for $C_{38}H_{38}N_6O_8$: 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 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]20 D = +104.0º (c: 5 mg·mL^{-1}, $CHCl_3$). ^{1}H NMR (500 MHz, d_6-DMSO): 2.56-2.61 (m, 2H, C-CH_2), 2.71-2.82 (m, 4H, C-CH_2), 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). ^{13}C 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 $C_{54}H_{60}N_8O_{18}$: 1108.4; found: 1109.4. $[M+H]^+$. Elemental analysis calcd. (%) for $C_{54}H_{60}N_8O_{18}$: 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 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]20 D = –103.9º (c: 5 mg·mL^{-1}, $CHCl_3$). ^{1}H NMR (500 MHz, d_6-DMSO): 2.56-2.61 (m, 2H, C-CH_2), 2.71-2.82 (m, 4H, C-CH_2), 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). ^{13}C 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 $C_{54}H_{60}N_8O_{18}$: 1108.4; found: 1109.4. $[M+H]^+$. Elemental

analysis calcd. (%) for $C_{54}H_{60}N_8O_{18}$: C, 58.48; H, 5.45; N, 10.10; found: C, 58.43; H, 5.44; N, 10.15.

Supplementary Figures

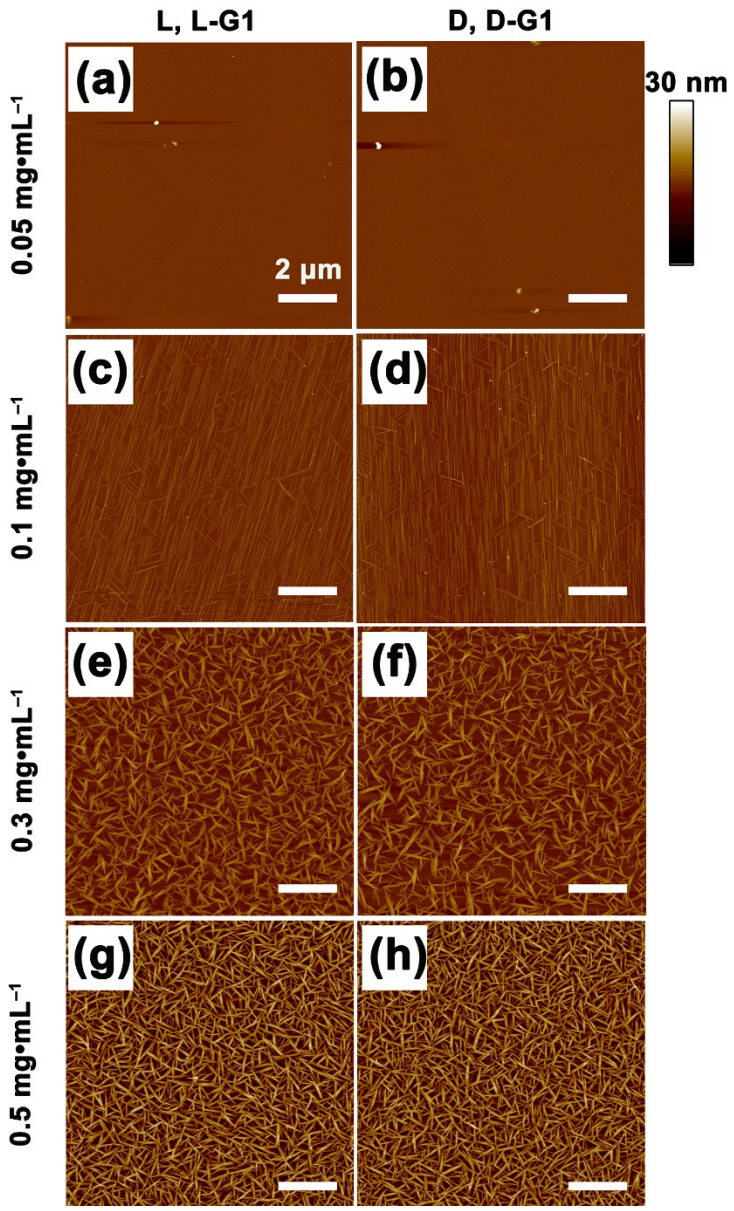

Figure S2. Self-assembled morphologies of L, L-G1 (a, c, e, g) and D, D-G1 (b, d, f, h) in chloroform on freshly cleaved mica surface. **(a, b)** 0.05 mg·mL^{-1}; **(c, d)** 0.1 mg·mL^{-1}; **(e, f)** 0.3 mg·mL^{-1}; **(g, h)** 0.5 mg·mL^{-1}, observed by AFM in a tapping mode. According to **(a, b)**, 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.

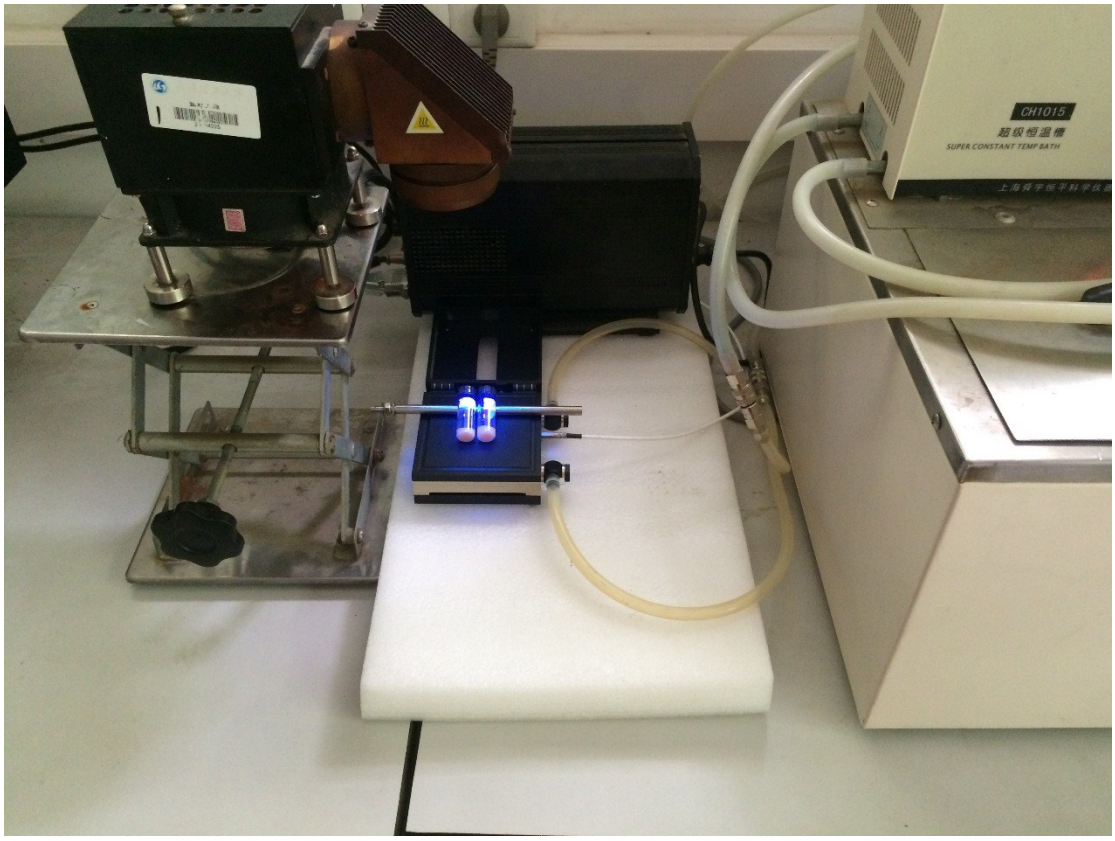

Figure S3. The apparatus used in the UV light irradiation experiment. The gel temperature was kept at 25 ºC by a temperature control plate. A variable power Xe lamp with a 365 nm band-pass filter (Perfect Light Crop., Beijing) was used as the UV light source.

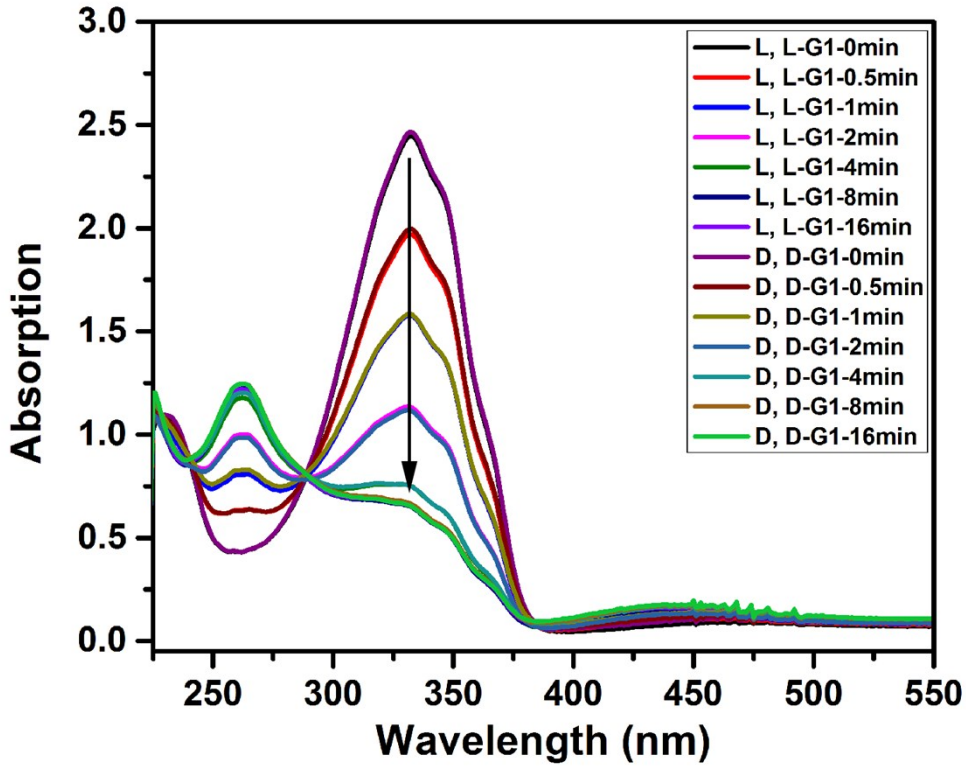

Figure S4. UV-Vis spectra of L, L-G1 and D, D-G1 in chloroform irradiated by UV light (λ: 365 nm, intensity: 5 mW·cm^{-2}) at different time intervals, the concentrations of solutions were 0.05 mg·mL^{-1}, obtained by Shimadzu UV-2500 spectrophotometer at 25 ºC. Identical absorption intensity changes 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.

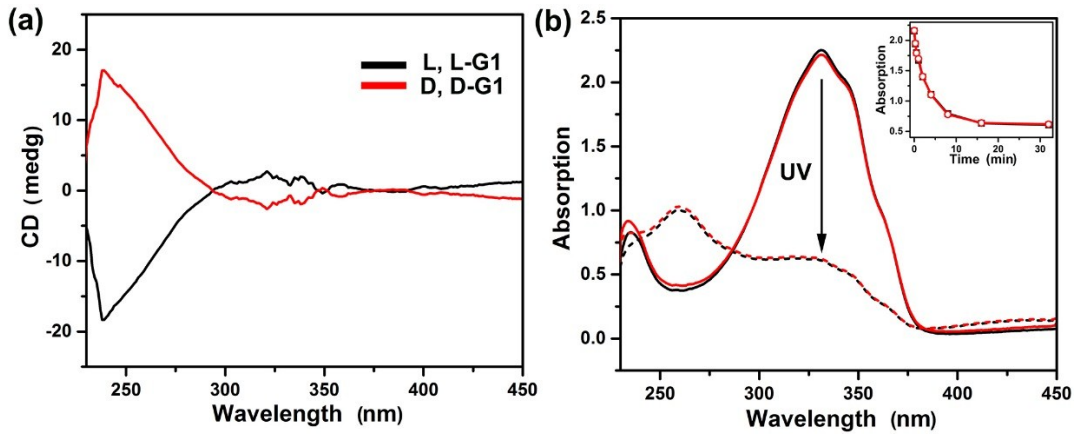

Figure S5. CD spectra (a) of L, L-G1 and D, D-G1 in chloroform/ methanol (v/v: 1/3, 0.05 mg·mL^{-1}), and UV-Vis (b) spectra of L, L-G1 and D, D-G1 in chloroform/ methanol (v/v: 1/3, 0.05 mg·mL^{-1}) before and after 15 min UV light (λ: 365 nm, intensity: 5 mW·cm^{-2}) irradiation. Black curves refer 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.

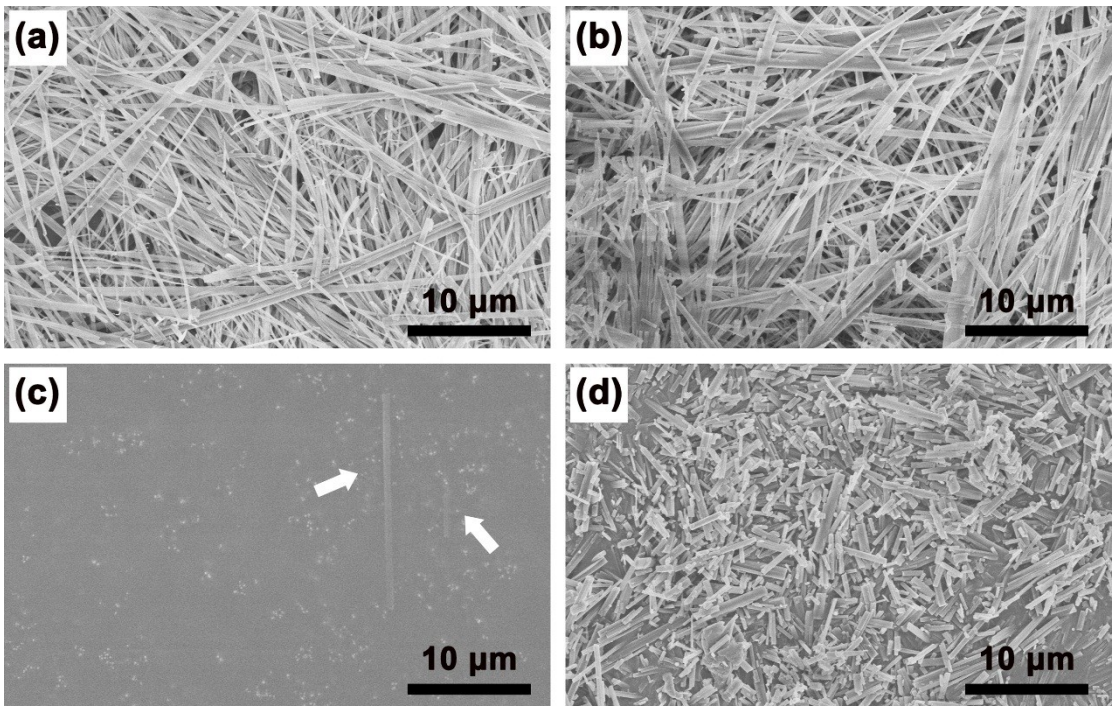

Figure S6. Self-assembled morphologies of L, L- (a, c) and D, D- (b, d) G1 gels before (a, b) and after (c, d) 30 min UV light irradiation (λ: 365 nm, intensity: 5 mW·cm^{-2}), observed by SEM on a larger scale. Gel formation condition: chloroform/methanol (v/v: 1/3, 5.0 mg·mL^{-1}). These data clearly indicated that significant chiral discrimination could also be observed on a large scale.

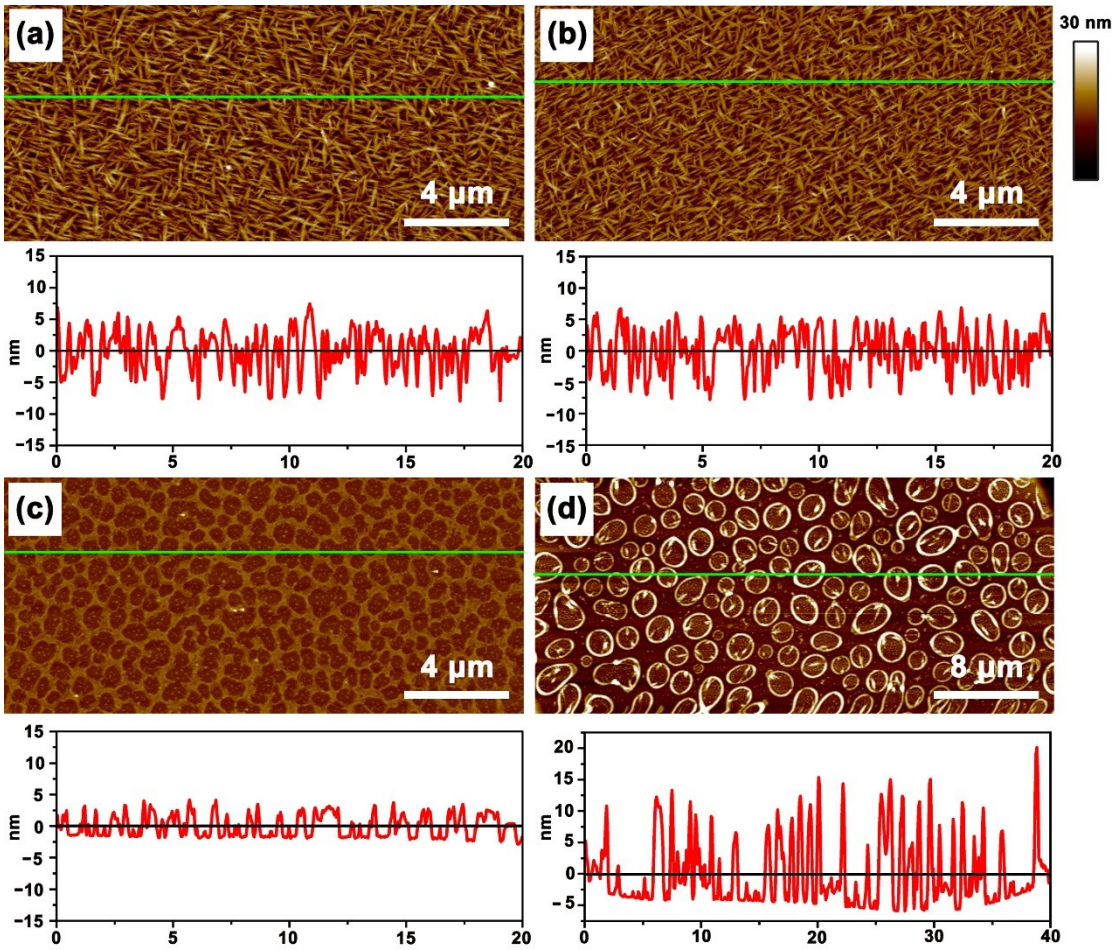

Figure S7. Self-assembled morphologies of L, L-G1 and D, D-G1 observed by AFM on a large scale. Self-assembled morphologies and section profiles along the green lines of L, L-**G1 (a, c)** and D, D-**G1 (b, d)** in chloroform (0.5 mg·mL^{-1}) before **(a, b)** and after **(c, d)** 15 min UV light irradiation (λ: 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.

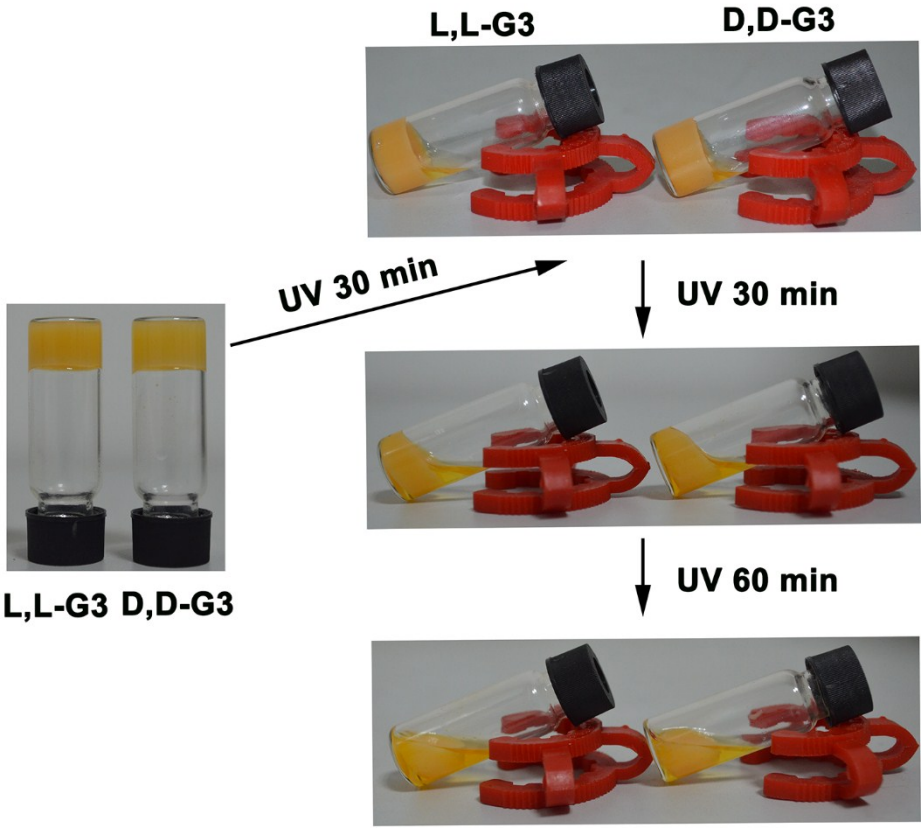

Figure S8. Photographs of L, L-G3 and D, D-G3 gels exposed to UV light irradiation at different time. Gel-sol transition of L, L-**G3** and D, D-**G3** gels (solvent: 1, 4-dioxane, concentration: 5 mg·mL^{-1}) upon UV light irradiation treatment. After 30 min, 60 min and 120 min of UV light irradiation (λ: 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 π–π 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.

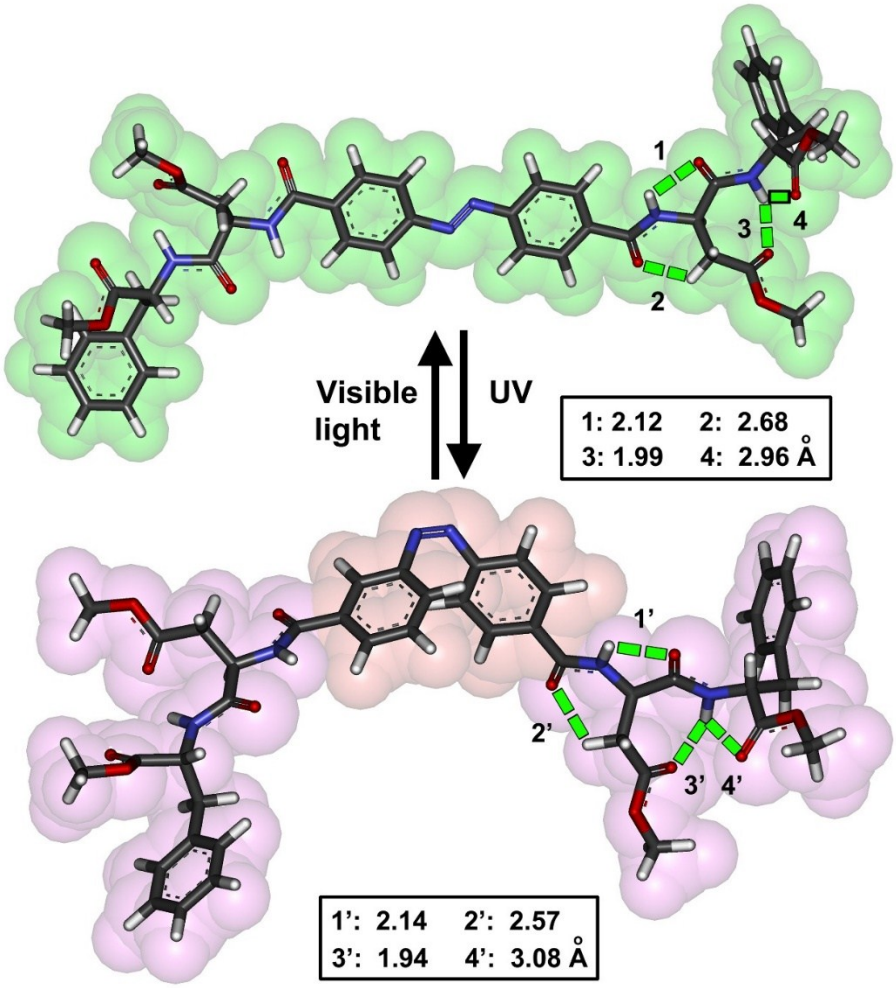

Figure S9. Optimized structures of *trans*- and *cis*-isomers of D, D-G1, obtained by density functional theory (DFT) calculations at the 6-311G level (Gaussian), using chloroform as a solvent parameter. Intramolecular H-bonds with different lengths are displayed by green dotted lines.

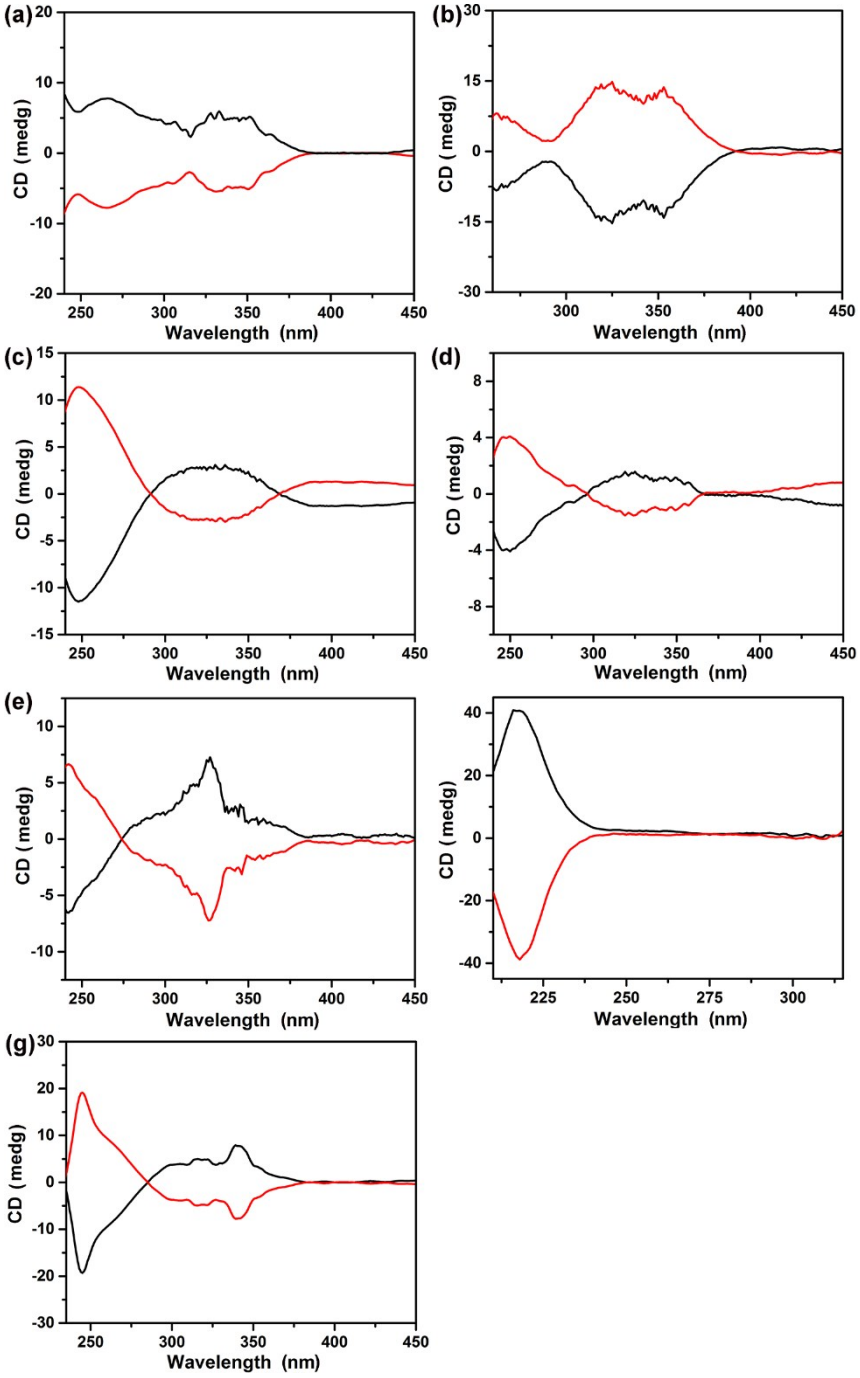

Figure S10. Circular dichroism (CD) spectra of gelators G2—G8. CD spectra of **(a)** L-**G2** and D-**G2** (CH_2Cl_2, 0.06 mg·mL^{-1}), **(b)** L, L-**G3** and D, D-**G3** (DMSO, 0.10 mg·mL^{-1}), **(c)** L, L-**G4** and D, D-**G4** ($CHCl_3$, 0.10 mg·mL^{-1}), **(d)** L, L-**G5** and D, D-**G5** (CH_2Cl_2, 0.04 mg·mL^{-1}), **(e)** L, L-**G6** and D, D-**G6** (CH_2Cl_2, 0.06 mg·mL^{-1}), **(f)** L-**G7** and D-**G7** (CH_3OH, 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 ($mg \cdot mL^{-1}$).

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

Solvent	G1	G2	G3	G4	G5	G6	G7	G8
$CHCl_3$	S	S	P	S	G (5.2)	P	P	S
CH_2Cl_2	P	S	P	S	G (4.8)	P	P	G (2.1)
CH_3OH	P	P	I	G (2.8)	S	P	I	G (4.2)
$CHCl_3/CH_3OH$ (1/3, v/v)	G (2.0)	S	I	G (3.8)	S	I	P	S
1, 4-dioxane	S	S	G (5.0)	P	S	S	S	P
Nitromethane	G (4.5)	G (4.8)	P	G (5.1)	S	I	S	G (2.6)
DMF	S	S	S	S	S	S	S	S
Acetone	P	S	I	P	P	S	P	P
Benzene	I	P	P	P	P	P	P	I
DMSO	S	S	S	S	S	S	S	S