MPTTF-Containing Tripeptide-Based Organogels: Receptor for 2, 4, 6-Trinitrophenol and Multiple Stimuli-Responsive Properties

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1. Instrumentation

Gelation study

A weight amount of the gelator **1** with or without TNP adding a measured volume of the solvent were placed in a sealed test tube and made a clear solution by heating. And then, the system left at room temperature. The transition temperatures ($T_{gel}$) were determined by ball-drop method.

NMR experiments

All solution state NMR studies were carried out on Bruker AV-300 Spectrometer (300 MHz for $^1$H and 75 MHz for $^{13}$C) and chemical shifts were referenced relative to tetramethylsilane ($\delta_H/\delta_C=0$).

FT-IR spectroscopy

IR spectra were recorded on a Shimadzu FT-IR Prestige-21 instrument with the KBr disk technique.

MALDI-TOF-MS spectrometry

Mass spectra were performed on a Shimadzu Axima CFR™ Plus using a 1,8,9-anthracenetriol (DITH) and β-phenylacrylic acid (CHCA) matrix.

Cyclic voltammetry

Cyclic voltammetry was performed with CHI660D instruments in a mixture of CH$_2$Cl$_2$ / CH$_3$CN (v:v = 1:1) with 0.1 M Bu$_4$NPF$_6$ as the supporting electrolyte and a scan rate of 100 mV$s^{-1}$. Counter and working electrodes were made of Pt and glass carbon, respectively, and an Ag/AgCl was used as the reference electrode. A small amount of the gel or CT gel was carefully put on the glass carbon electrode, which was left in air for 24h.

UV-vis spectroscopy

UV-vis spectra were recorded on a Hitachi U-3010 spectrophotometer.

Circular dichroism (CD) spectroscopy

CD spectra were obtained on Chirascan spectrometer using a 1 mm path-length cell.

Atomic force microscopy (AFM)

For AFM experiments, 10 μL of sample solution (diluted gels) was drop-casted onto a freshly cleaved mica surface. Each sample was air-dried 48 h in a dust-free environment prior to AFM imaging. The images were obtained by scanning the mica surfaces in air under ambient conditions.
using Agilent-5500 in tapping mode.

**Field emission scanning electron microscopy**

The gel samples were placed on silicon wafer, and dried for 24 h under room temperature before imaging. A layer of gold was sputtered on top to form a conducting surface and finally the specimen was transferred into the Field Emission Scanning Electron Microscope (FE-SEM, Joel Scanning Microscope-JSM-6700F).

**Small-angle X-ray diffracting**

Small-angle X-ray scattering (SAXS) measurements were carried out at 298 K on a beamline 1W2A synchrotron radiation X-ray small angle system at Beijing Synchrotron Radiation Facility ($\lambda = 1.54\text{Å}$).

**Wide-angle x-ray diffraction**

Wide-angle X-ray diffracting (WAXRD) measurements were carried out at 298 K on the glass-sustained xerogel films and recorded on a Bruker D8/ADVANCE X-ray diffractmeter (Germany) with radiation ($\lambda = 1.54\text{Å}$) at Chang Chun Institute of Applied Chemistry Chinese Academy of Sciences.
2. Synthetic procedure and Characterization

All the amino and carboxyl coupling reactions were carried out using the standard EDCI/HOBt method.\(^1\) Firstly, tert-butyloxycarbonyl (Boc)-protected L-amino acids was coupled with the methyl ester protected L-amino acids by using EDCI (1.2 equiv.) and HOBt (1.2 equiv.) in dry dichloromethane. After reaction finishing, the coupled product was washed sequentially with water, dilute NaOH and water to neutrality. The crude product was purified by flash chromatography (SiO\(_2\), 100-200mesh). The product was subjected to hydrolysis with 1 M NaOH solution in methanol followed by workup with 1 M HCl. Adding in the ethyl acetate and the organic part was dried over anhydrous sodium sulphate and the solvent was evaporated to get the crude coupled product. The free acid terminus of the L-dipeptide was further coupled with n-dodecylamine by using EDCI/HOBt, similarly to the procedure described above. Then, the corresponding N-Boc-protected of the product was subjected to deprotection by TFA (20 equiv.) in dry DCM. After stirring for 2 h, solvents were removed on a rotary evaporator. The residue obtained was repeatedly dissolved in dichloromethane and the solvent evaporated to yield the crude trifluoroacetate salt, which was taken in ethyl acetate. The EtOAc part was thoroughly washed with saturated sodium bicarbonate solution and brine to neutrality. The organic part was dried over anhydrous sodium sulphate and concentrated to get the corresponding amine which was used in the next step without further purification. Following a similar method, monochloroacetic acid was coupled with the corresponding amines by using EDCI/HOBt in dry dichloromethane stirring at room temperature for 1 d. Collecting the generated white solids and recrystallization from methanol to afford the corresponding intermediate products. Finally, the got intermediate compounds were reacted with MPTTF \(^2\) by using Cs\(_2\)CO\(_3\) as a base in dry THF/CH\(_3\)CN. The resultant reaction mixture was then filtered and the filtrate was concentrated in a rotary evaporator. The crude products were purified by flash chromatography (SiO\(_2\), 100-200mesh) with MeOH/CH\(_3\)Cl\(_2\) as the eluents, respectively.

Reference:
Characterization of intermediate compounds 10

Characterization of 10a (BOC-Gly-Phe-NH-C$_{12}$H$_{25}$)

White solid. m.p. 108-109°C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.88 (t, $J = 6$ Hz, 3H), 1.15-1.37 (m, 27 H), 1.73 (br, 2H), 3.02-3.08 (m, 2H), 3.10-3.23 (m, 2H), 3.32 (s, 2H), 4.58 (q, $J = 9$ Hz, 1H), 5.98 (t, $J = 4.5$ Hz, 1H), 7.21-7.31 (m, 5H), 7.82 (d, $J = 9$ Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 172.70, 170.58, 159.70, 137.02, 129.29, 128.65, 126.96, 79.84, 54.57, 44.53, 39.58, 38.46, 31.98, 29.71, 29.66, 29.58, 29.42, 29.34, 29.31, 29.26, 26.86, 22.76, 14.19; MALDI-TOF MS m/z Caled for C$_{28}$H$_{47}$N$_3$O$_4$: 489.36. Found: 390.4 ([M-Boc+2H]$,^+$, 100).

Characterization of 10b (BOC-Leu-Phe-NH-C$_{12}$H$_{25}$)

White solid. m.p. 155-156°C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.88 (t, $J = 6$ Hz, 3H), 1.22-1.36 (m, 36H), 1.50-1.56 (m, 2H), 3.08-3.18 (m, 3H), 3.26-3.34 (m, 2H), 4.52 (q, $J = 9$ Hz, 1H), 5.63 (t, $J = 4.5$ Hz, 1H), 7.21-7.33 (m, 5H), 7.40 (t, $J = 5.7$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 169.19, 159.80, 158.93, 136.19, 129.23, 128.71, 127.10, 80.55, 55.24, 39.75, 39.59, 38.20, 31.86, 29.57, 29.44, 29.29, 29.16, 26.79, 26.70, 22.63, 14.06; MALDI-TOF MS m/z Caled for C$_{32}$H$_{55}$N$_3$O$_4$: 449.42. Found: 450.3 ([M+1]$^+$, 100).

Characterization of 10c (BOC-Phe-Phe-NH-C$_{12}$H$_{25}$)

White solid. m.p. 165-166°C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.88 (t, $J = 6$ Hz, 3H), 1.22-1.36 (m,
27H), 1.50-1.58 (m, 2H), 3.09-3.17 (m, 2H), 3.29 (q, J = 6 Hz, 4H), 4.52 (q, J = 6 Hz, 2H), 5.62 (t, J = 5.4 Hz, 1H), 7.21-7.33 (m, 10H), 7.40 (t, J = 6 Hz, 1H), 8.05 (d, J = 8.7 Hz, 1H); \(^{13}\text{C} \text{ NMR } (75 \text{ MHz, CDCl}_3) \delta 169.29, 159.91, 159.04, 136.30, 129.34, 128.83, 127.22, 79.58, 55.36, 39.86, 39.70, 38.31, 31.97, 29.69, 29.68, 29.64, 29.56, 29.40, 29.27, 26.90, 26.82, 22.74, 14.17; \text{MALDI-TOF MS } m/z \text{ Calcd for C}_{35}H_{53}N_3O_4: 571.41. \text{Found: 571.7 ([M]+, 100).}

Characterization of 10d (BOC-Leu-Leu-NH-C\textsubscript{12}H\textsubscript{25})

Colourless oil liquid. \(^1\text{H} \text{ NMR } (300 \text{ MHz, CDCl}_3) \delta 0.86-0.93 (m, 15H), 1.25-1.37 (m, 20H), 1.44 (s, 9H), 1.55-1.66 (m, 6H), 3.12-3.29 (m, 2H), 4.18 (br, 1H), 4.49 (br, 1H), 5.42 (br, 1H), 6.97 (t, J = 6 Hz, 1H), 7.13 (t, J = 6 Hz, 1H); \(^{13}\text{C} \text{ NMR } (75 \text{ MHz, CDCl}_3) \delta 172.87, 171.83, 155.82, 79.98, 53.28, 51.81, 41.30, 40.99, 39.59, 31.93, 29.68, 29.66, 29.60, 29.49, 29.37, 28.34, 26.97, 24.76, 22.94, 22.70, 22.15, 14.13; \text{MALDI-TOF MS } m/z \text{ Calcd for C}_{29}H_{57}N_3O_4: 511.43. \text{Found: 511.8 ([M]+, 100).}

Characterization of 10e (BOC-Gly-Leu-NH-C\textsubscript{12}H\textsubscript{25})

White solid. m.p. 121-122°C; \(^1\text{H} \text{ NMR } (300 \text{ MHz, CDCl}_3) \delta 0.86-0.94 (m, 9H), 1.25-1.37 (m, 19H), 1.45-1.51 (m, 11H), 1.58-1.66 (m, 2H), 3.12-3.31 (m, 2H), 3.80 (s, 2H), 4.43 (q, J = 8.4 Hz, 1H), 5.34 (br, 1H), 6.54 (t, J = 8.7 Hz, 1H), 6.81 (t, J = 8.4 Hz, 1H); \(^{13}\text{C} \text{ NMR } (75 \text{ MHz, CDCl}_3) \delta 168.21, 166.19, 155.71, 76.95, 48.37, 40.96, 37.72, 36.28, 28.51, 26.25, 26.20, 26.14, 26.00, 25.95, 25.88, 24.87, 23.50, 21.35, 19.49, 19.28, 18.68, 10.71; \text{MALDI-TOF MS } m/z \text{ Calcd for C}_{25}H_{49}N_3O_4: 455.37. \text{Found: 399.7 ([M-isobutyl+2H]+, 100).}

Characterization of 10f (BOC-Gly-Gly-NH-C\textsubscript{12}H\textsubscript{25})

White solid. m.p. 78-79°C; \(^1\text{H} \text{ NMR } (300 \text{ MHz, CDCl}_3) \delta 0.89 (t, J = 6 Hz, 3H), 1.24-1.35 (m, 18H), 1.46-1.53 (s, 11H), 3.24 (q, J = 6.6 Hz, 2H), 3.83 (d, J = 3.9 Hz, 2H), 3.95 (d, J = 5.1 Hz, 2H), 5.43 (br, 1H), 6.60 (br, 1H), 7.12 (br, 1H); \(^{13}\text{C} \text{ NMR } (75 \text{ MHz, CDCl}_3) \delta 170.05, 168.65, 156.41, 80.48, 44.53, 43.15, 39.80, 31.95, 29.69, 29.58, 29.46, 29.38, 29.34, 28.35, 26.95, 22.72, 14.15; \text{MALDI-TOF MS } m/z \text{ Calcd for C}_{21}H_{41}N_3O_4: 399.31. \text{Found: 398.6 ([M-1]+, 100).}

Cleavage of the N-Boc protecting group and get compounds 9

Trifluoroacetic acid (TFA, 10 mL) was added to a solution of the corresponding N-Boc-protected compound (ca. 2 g) in dichloromethane (15 mL). The solution was stirred at room temperature for 2 h and evaporated. The residue obtained was repeatedly dissolved in dichloromethane and the solvent evaporated to yield the crude trifluoroacetate salt, which was redissolved in
dichloromethane (60 mL) and washed with saturated aqueous NaHCO₃ (3 x 40 mL) and brine to neutrality. After drying and filtering, evaporation of the solvent afforded the corresponding amine which was used in the next step without further purification.

Characterization of intermediate compounds 8

Characterization of 8a (Chloracetyl-Gly-Phe-NH-C₁₂H₂₅)
White solid. m.p. 128-129°C; ¹H NMR (300 MHz, d₆-DMSO) δ 0.85 (t, J = 6 Hz, 3H), 1.24-1.40 (m, 20H), 2.73-3.11 (m, 4H), 3.6-3.82 (m, 2H), 4.11 (s, 2H), 4.41-4.49 (m, 1H), 7.16-7.27 (m, 5H), 7.92 (t, J = 5.1 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 8.35 (t, J = 5.4 Hz, 1H); ¹³C NMR (75 MHz, d₆-DMSO) δ 170.28, 167.84, 166.22, 137.67, 129.10, 127.86, 126.22, 54.08, 42.43, 42.14, 38.51, 37.95, 31.29, 29.05, 29.01, 28.96, 28.89, 28.71, 26.28, 22.08, 13.93; MALDI-TOF MS m/z Calcd for C₂₅H₄₀ClN₃O₃: 465.28. Found: 389.5 ([M-chloracetyl+2H]⁺, 100).

Characterization of 8b (Chloracetyl-Leu-Phe-NH-C₁₂H₂₅)
White solid. m.p. 162-163°C; ¹H NMR (300 MHz, d₆-DMSO) δ 0.80-0.86 (m, 9H), 1.24-1.54 (m, 23H), 2.71-3.08 (m, 4H), 4.08 (s, 2H), 4.26-4.39 (m, 1H), 4.42-4.46 (m, 1H), 7.12-7.22 (m, 5H), 7.71 (t, J = 5.1 Hz, 1H), 8.12 (d, J = 7.2 Hz, 1H), 8.28 (t, J = 6.3 Hz, 1H); ¹³C NMR (75 MHz, d₆-DMSO) δ 171.14, 170.27, 165.72, 137.70, 129.11, 127.97, 126.18, 53.94, 51.41, 42.54, 40.88, 38.43, 37.65, 31.28, 29.05, 29.00, 28.87, 28.74, 28.70, 26.22, 24.06, 22.92, 22.54, 22.08, 21.66, 13.93; MALDI-TOF MS m/z Calcd for C₂₉H₄₈ClN₃O₃: 521.34. Found: 521.3 ([M]⁺, 100).

Characterization of 8c (Chloracetyl-Phe-Phe-NH-C₁₂H₂₅)
White solid. m.p. 167-168°C; ¹H NMR (300 MHz, d₆-DMSO) δ 0.85 (t, J = 6.3 Hz, 3H), 1.23-1.41 (m, 20H), 2.65-3.10 (m, 6H), 4.00 (s, 2H), 4.42-4.59 (m, 2H), 7.15-7.27 (m, 10H), 7.81 (t, J = 5.4 Hz, 1H), 8.25-8.33 (m, 2H); ¹³C NMR (75 MHz, d₆-DMSO) δ 170.24, 170.18, 165.48, 137.63, 137.31, 129.23, 129.16, 128.02, 127.88, 126.25, 54.12, 53.91, 42.42, 38.47, 37.54, 31.30, 29.07, 29.02, 28.92, 28.77, 28.72, 26.27, 22.09, 13.95; MALDI-TOF MS m/z Calcd for C₃₂H₄₆ClN₃O₃: 555.32. Found: 555.2 ([M]⁺, 100).

Characterization of 8d (Chloracetyl-Leu-Leu-NH-C₁₂H₂₅)
White solid. m.p. 157-158°C; ¹H NMR (300 MHz, d₆-DMSO) δ 0.82-0.89 (m, 15H), 1.24 (br, 18H), 1.36 (t, J = 6 Hz, 2H), 1.41-1.46 (m, 4H), 1.51-1.62 (m, 2H), 2.93-3.10 (m, 2H), 4.10 (s, 2H), 4.24 (q, J = 8.4 Hz, 1H), 4.33 (q, J = 7.5 Hz, 1H), 7.75 (t, J = 8.4 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 8.31 (d, J = 8.1 Hz, 1H); ¹³C NMR (75 MHz, d₆-DMSO) δ 171.38, 171.15, 165.74, 51.35, 51.10, 42.54, 40.98, 40.90, 38.32, 31.28, 29.04, 28.99, 28.92, 28.70, 26.20, 24.18, 24.12, 22.98,
Characterization of 8e (Chloracetyl-Gly-Leu-NH-C$_{12}$H$_{25}$)
White solid. m.p. 140-141°C; $^1$H NMR (300 MHz, $d_6$-DMSO) $\delta$ 0.82-0.89 (m, 9H), 1.24 (br, 18H), 1.36-1.45 (m, 3H), 1.48-1.60 (m, 2H), 2.91-3.11 (m, 2H), 3.76-3.79 (m, 2H), 4.13 (s, 2H), 4.25 (q, $J = 8.1$ Hz, 1H), 7.88 (t, $J = 5.4$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 8.39 (t, $J = 5.4$ Hz, 1H); $^{13}$C NMR (75 MHz, $d_6$-DMSO) $\delta$ 171.46, 167.89, 166.10, 51.03, 42.47, 42.22, 41.17, 38.44, 31.27, 29.02, 28.98, 28.68, 26.26, 24.18, 24.16, 22.94, 22.89, 22.08, 22.06, 21.69, 21.67, 13.93; MALDI-TOF MS m/z Calcd for C$_{26}$H$_{50}$ClN$_3$O$_3$: 487.35. Found: 488.6 ([M+1]$^+$, 100).

Characterization of 8f (Chloracetyl-Gly-Gly-NH-C$_{12}$H$_{25}$)
White solid. m.p. 212-213°C; $^1$H NMR (300 MHz, $d_6$-DMSO) $\delta$ 0.86 (t, $J = 6$ Hz, 3H), 1.24 (br, 18H), 1.36-1.41 (m, 2H), 3.04 (q, $J = 6.6$ Hz, 2H), 3.66 (s, 2H), 3.78 (s, 2H), 4.14 (s, 2H), 7.69 (br, 1H), 8.18 (br, 1H), 8.46 (br, 1H); $^{13}$C NMR (75 MHz, $d_6$-DMSO) $\delta$ 168.37, 168.13, 165.35, 42.55, 42.46, 42.02, 38.35, 31.38, 29.11, 28.82, 27.37, 26.55, 26.36, 22.15, 13.94; MALDI-TOF MS m/z Calcd for C$_{18}$H$_{34}$ClN$_3$O$_3$: 379.23. Found: 379.5 ([M]$^+$, 100).

Characterization of gelators 1-6
Characterization of 1 (MPTTF-CH$_2$CO-Gly-Phe-NH-C$_{12}$H$_{25}$)
Yellow solid. m.p. 124-125°C; $^1$H NMR (300 MHz, $d_6$-DMSO) $\delta$ 0.83-0.90 (m, 9H), 1.24 (br, 18H), 1.29-1.33 (m, 2H), 1.35-1.45 (m, 4H), 1.50-1.59 (m, 4H), 2.72-2.83 (m, 2H), 2.85 (t, $J = 6.9$ Hz, 4H), 2.93-3.06 (m, 2H), 3.57-3.80 (m, 2H), 4.40-4.47 (m, 1H), 4.58 (s, 2H), 6.76 (s, 2H), 7.17-7.27 (m, 5H), 7.87 (t, $J = 5.1$ Hz, 1H), 8.17-8.22 (m, 2H); $^{13}$C NMR (75 MHz, $d_6$-DMSO) $\delta$ 170.65, 168.44, 167.82, 138.00, 129.36, 128.30, 126.99, 126.50, 121.06, 120.98, 117.43, 114.96, 108.02, 54.36, 52.60, 42.31, 38.12, 35.30, 31.60, 29.39, 29.34, 29.16, 29.03, 26.62, 22.40, 21.17, 14.24, 13.68; MALDI-TOF MS m/z Calcd for C$_{41}$H$_{60}$N$_4$O$_3$S$_6$: 848.30. Found: 848.3 ([M]$^+$, 100); elemental analysis calcd for C$_{41}$H$_{60}$N$_4$O$_3$S$_6$: C 57.98, H 7.12, N 6.60; found: C 58.15, H 7.43, N 6.31.

Characterization of 2 (MPTTF-CH$_2$CO-Leu-Phe-NH-C$_{12}$H$_{25}$)
Yellow solid. m.p. 139-140°C; $^1$H NMR (300 MHz, $d_6$-DMSO) $\delta$ 0.83-0.90 (m, 15H), 1.24 (br, 19H), 1.35-1.45 (m, 6H), 1.50-1.59 (m, 6H), 2.63-2.80 (m, 2H), 2.85 (t, $J = 6.9$ Hz, 4H), 2.93-3.02 (m, 2H), 4.13-4.23 (m, 1H), 4.37-4.46 (m, 1H), 4.55 (s, 2H), 6.72 (s, 1H), 6.74 (s, 1H), 7.17-7.23 (m, 5H), 7.70 (t, $J = 5.4$ Hz, 1H), 8.02 (d, $J = 8.1$ Hz, 1H), 8.23 (d, $J = 7.2$ Hz, 1H); $^{13}$C NMR (75
MHz, $d_6$-DMSO) $\delta$ 171.89, 170.69, 167.80, 138.82, 138.34, 129.67, 128.56, 127.28, 126.77, 117.66, 115.21, 108.26, 54.31, 52.24, 41.44, 38.09, 35.61, 31.91, 29.71, 29.66, 29.44, 29.40, 29.35, 27.05, 26.94, 24.59, 24.33, 23.44, 22.99, 22.71, 22.31, 21.42, 14.55, 13.99; MALDI-TOF MS m/z Calcd for C$_{45}$H$_{68}$N$_{4}$O$_{3}$S$_{6}$: 903.36. Found: 902.3 ([M-1]$^+$, 100); elemental analysis calcd for C$_{45}$H$_{68}$N$_{4}$O$_{3}$S$_{6}$: C 59.69, H 7.57, N 6.19; found: C 59.97, H 7.93, N 6.54.

Characterization of 3 (MPTTF-CH$_2$CO-Phe-Phe-NH-C$_{12}$H$_{25}$)

Yellow solid. m.p. 157-158°C; $^1$H NMR (300 MHz, $d_6$-DMSO) $\delta$ 0.83-0.90 (m, 9H), 1.23 (br, 18H), 1.27-1.33 (m, 2H), 1.35-1.45 (m, 4H), 1.50-1.59 (m, 4H), 2.69-2.80 (m, 2H), 2.85 (t, $J$ = 6.9 Hz, 4H), 2.91-3.07 (m, 4H), 2.95-3.45 (s, 4H), 6.60 (s, 2H), 7.13-7.27 (m, 10H), 7.79 (t, $J$ = 5.4 Hz, 1H), 8.16 (d, $J$ = 8.1 Hz, 1H), 8.26 (t, $J$ = 8.1 Hz, 1H); $^{13}$C NMR (75 MHz, $d_6$-DMSO) $\delta$ 170.86, 167.27, 138.23, 137.86, 129.81, 129.72, 128.60, 128.54, 127.30, 126.80, 121.37, 117.66, 115.04, 108.42, 54.60, 54.40, 38.40, 38.20, 35.60, 31.89, 29.67, 29.62, 29.48, 29.36, 29.31, 26.89, 21.47, 14.53, 13.97; MALDI-TOF MS m/z Calcd for C$_{48}$H$_{66}$N$_{4}$O$_{3}$S$_{6}$: 938.35. Found: 939.5 ([M+1]$^+$, 100); elemental analysis calcd for C$_{48}$H$_{66}$N$_{4}$O$_{3}$S$_{6}$: C 61.37, H 7.08, N 5.96; found: C 61.71, H 7.42, N 5.65.

Characterization of 4 (MPTTF-CH$_2$CO-Leu-Leu-NH-C$_{12}$H$_{25}$)

Yellow solid. m.p. 131-132°C; $^1$H NMR (300 MHz, $d_6$-DMSO) $\delta$ 0.81-0.90 (m, 21H), 1.23 (br, 18H), 1.30-1.45 (m, 8H), 1.49-1.63 (m, 8H), 1.49-1.63 (m, 8H), 2.85 (t, $J$ = 6.9 Hz, 4H), 2.92-3.07 (m, 2H), 4.18-4.28 (m, 2H), 4.58 (s, 2H), 6.76 (s, 2H), 7.68 (t, $J$ = 5.4 Hz, 1H), 7.93 (d, $J$ = 8.4 Hz, 1H), 8.26 (t, $J$ = 7.8 Hz, 1H); $^{13}$C NMR (75 MHz, $d_6$-DMSO) $\delta$ 174.28, 171.99, 167.68, 127.13, 121.30, 117.69, 115.20, 108.33, 52.14, 51.58, 41.46, 35.59, 31.90, 29.66, 29.65, 29.64, 29.34, 29.32, 26.89, 26.78, 24.83, 24.74, 23.57, 23.46, 22.72, 22.68, 22.26, 21.47, 14.55, 13.97; MALDI-TOF MS m/z Calcd for C$_{42}$H$_{70}$N$_{4}$O$_{3}$S$_{6}$: 870.38. Found: 869.3 ([M+1]$^+$, 100); elemental analysis calcd for C$_{42}$H$_{70}$N$_{4}$O$_{3}$S$_{6}$: C 57.89, H 8.10, N 6.43; found: C 58.12, H 8.35, N 6.15.

Characterization of 5 (MPTTF-CH$_2$CO-Gly-Leu-NH-C$_{12}$H$_{25}$)

Yellow solid. m.p. 137-138°C; $^1$H NMR (300 MHz, $d_6$-DMSO) $\delta$ 0.81-0.90 (m, 15H), 1.24 (br, 18H), 1.33-1.45 (m, 7H), 1.50-1.59 (m, 6H), 2.85 (t, $J$ = 6.9 Hz, 4H), 2.91-3.06 (m, 2H), 3.70-3.82 (m, 2H), 4.20-4.27 (m, 1H), 4.61 (s, 2H), 6.78 (s, 2H), 7.82 (t, $J$ = 5.1 Hz, 1H), 8.02 (d, $J$ = 8.1 Hz, 1H), 8.25 (t, $J$ = 5.1 Hz, 1H); $^{13}$C NMR (75 MHz, $d_6$-DMSO) $\delta$ 172.01, 168.74, 168.28, 127.29, 121.34, 117.71, 115.15, 108.37, 51.57, 42.73, 41.63, 35.59, 31.89, 29.63, 29.49, 29.32, 26.91, 26.87, 26.85, 24.72, 23.51, 22.69, 22.26, 22.22, 21.47, 14.52, 13.97; MALDI-TOF MS m/z Calcd for C$_{38}$H$_{62}$N$_{4}$O$_{3}$S$_{6}$: 814.31. Found: 813.5 ([M+1]$^+$, 100); elemental analysis calcd for
Characterization of 6 (MPTTF-CH$_2$CO-Gly-Gly-NH-C$_{12}$H$_{25}$)

Yellow solid. m.p. 144-145°C; $^1$H NMR (300 MHz, $d_6$-DMSO) δ 0.83-0.90 (m, 9H), 1.24 (br, 18H), 1.33-1.45 (m, 6H), 1.50-1.59 (m, 4H), 2.85 (t, $J = 6.9$ Hz, 4H), 3.00 (q, $J = 6.3$ Hz, 2H), 3.65 (d, $J = 5.7$ Hz, 2H), 3.74 (d, $J = 5.4$ Hz, 2H), 4.62 (s, 2H), 6.79 (s, 2H), 7.61 (t, $J = 5.1$ Hz, 1H), 8.20 (t, $J = 5.7$ Hz, 1H), 8.36 (t, $J = 5.1$ Hz, 1H); $^{13}$C NMR (75 MHz, $d_6$-DMSO) δ 169.34, 168.88, 168.63, 127.23, 121.29, 117.60, 115.32, 108.18, 52.90, 43.02, 42.57, 35.59, 31.90, 29.70, 29.66, 29.58, 29.39, 29.34, 27.02, 22.70, 21.47, 14.54, 13.98; MALDI-TOF MS m/z Calcd for C$_{34}$H$_{54}$N$_4$O$_3$S$_6$: 758.25. Found: 757.3 ([M-1]$^+$, 100); elemental analysis calcd for C$_{34}$H$_{54}$N$_4$O$_3$S$_6$: C 53.79, H 7.17, N 7.38; found: C 54.05, H 7.41, N 7.03.

3. The gelation properties.

Table S1 Gelation tests for 1-6.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylocyclohexane</td>
<td>6.5(TG)$^a$</td>
<td>15.8(TG)</td>
<td>8.3(TG)</td>
<td>S</td>
<td>8.7(TG)</td>
<td>8.9(TG)</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>5.1(TG)</td>
<td>13.8(TG)</td>
<td>6.6(TG)</td>
<td>S</td>
<td>IS</td>
<td>IS</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>IS</td>
<td>IS</td>
<td>7.2(TG)</td>
<td>S</td>
<td>S</td>
<td>5.7(TG)</td>
</tr>
<tr>
<td>Benzenne</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>4.8(TG)</td>
</tr>
<tr>
<td>Toluene</td>
<td>S</td>
<td>S</td>
<td>5.8(TG)</td>
<td>S</td>
<td>S</td>
<td>3.6(TG)</td>
</tr>
<tr>
<td>Chloroformene</td>
<td>S</td>
<td>S</td>
<td>11.5(TG)</td>
<td>S</td>
<td>S</td>
<td>4.1(TG)</td>
</tr>
<tr>
<td>Xylene</td>
<td>S</td>
<td>S</td>
<td>6.4(TG)</td>
<td>S</td>
<td>S</td>
<td>6.0(TG)</td>
</tr>
<tr>
<td>Chloroformene</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<tr>
<td>CHCl$_3$</td>
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<tr>
<td>CCl$_4$</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<tr>
<td>CH$_3$CN</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>3.2(OG)</td>
</tr>
<tr>
<td>EA</td>
<td>PG</td>
<td>S</td>
<td>P</td>
<td>S</td>
<td>S</td>
<td>1.8(OG)</td>
</tr>
<tr>
<td>THF</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Methanol</td>
<td>P</td>
<td>13.8(OG)</td>
<td>P</td>
<td>P</td>
<td>S</td>
<td>P</td>
</tr>
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<td>Ethanol</td>
<td>S</td>
<td>13.8(OG)</td>
<td>P</td>
<td>S</td>
<td>S</td>
<td>4.8(OG)</td>
</tr>
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<td>Acetone</td>
<td>P</td>
<td>S</td>
<td>P</td>
<td>S</td>
<td>S</td>
<td>29(OG)</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>IS</td>
<td>sS</td>
<td>IS</td>
<td>S</td>
<td>PG</td>
<td>IS</td>
</tr>
<tr>
<td>DMF</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>DMSO</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Kerosene</td>
<td>sS</td>
<td>24(OG)</td>
<td>1.7(OG)</td>
<td>16(OG)</td>
<td>2.2(OG)</td>
<td>IS</td>
</tr>
</tbody>
</table>

$^a$OG = opaque gel; TG = transparent gel; PG = part gel; P = precipitation; 
S = soluble; IS = insoluble; sS = slight soluble.

$^b$CGC = the critical gelation concentrations (mg/mL) at room temperature.
4. Gelation abilities in other solvents

Figure S1. The photographs of gelators (a) 2 and 6 in ethanol, (b) 6 in acetonitrile and (c) 6 in ethyl acetate.

5. FE-SEM images

Figure S2. FE-SEM images of 1, 2, 3, 5 and 6 xerogels obtained from cyclohexane (a-e) and 5 and 6 xerogels from toluene (f-g).
6. WAXRD studies

Figure S3. WAXRD patterns of xerogels of 3 (-Phe-Phe-) from cyclohexane (a) and toluene (b).

7. Data from FT-IR and UV-Vis

Table S2 Summary data of FT-IR and UV-Vis spectra of 3 (-Phe-Phe-) in DMSO solution and xerogel from cyclohexane and toluene, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$\nu \text{N-H (cm}^{-1}\text{)}$</th>
<th>$\nu \text{C=O (cm}^{-1}\text{)}$</th>
<th>$\delta \text{N-H (cm}^{-1}\text{)}$</th>
<th>UV-Vis (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO solution</td>
<td>3411, 3281</td>
<td>1664</td>
<td>1550</td>
<td>291, 325, 455</td>
</tr>
<tr>
<td>xerogel from toluene</td>
<td>3275</td>
<td>1638</td>
<td>1553</td>
<td>296, 329, 480</td>
</tr>
<tr>
<td>xerogel from cyclohexane</td>
<td>3275</td>
<td>1638</td>
<td>1554</td>
<td>296, 328, 481</td>
</tr>
</tbody>
</table>

8. Anions responsive

Figure S4. Photographs of the 3 (-Phe-Phe-) gel (toluene, 6 mg/mL) upon the addition of 3.0 equiv. of each anion. From left to right: native gel, + F\textsuperscript{-}, Cl\textsuperscript{-}, H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-}, Br\textsuperscript{-}, I\textsuperscript{-}, HSO\textsubscript{4}\textsuperscript{-}, AcO\textsuperscript{-}.
Figure S5. Reversible sol–gel phase transition of the 3 (-Phe-Phe-) gel in cyclohexane trigged by anions and water.

Figure S6. Reversible sol–gel phase transition of the 6 (-Gly-Gly-) gel in CH$_3$CN trigged by anions and methanol.

9. UV-Vis spectra changes by addition of anions

Figure S7. UV-Vis spectra of 3 (-Phe-Phe-) in DMSO (5×10$^{-5}$ M) with addition of 3.0 equiv. different anions, respectively.
10. CV curves

![Cyclic voltammograms of 1-6 (1 × 10\(^{-3}\)M) in CH\(_2\)Cl\(_2\)-CH\(_3\)CN (1 : 1, v/v) containing 0.1 M Bu\(_4\)NPF\(_6\). Scan rate was 100 mV s\(^{-1}\).](image)

**Figure S8.** Cyclic voltammograms of 1-6 (1 × 10\(^{-3}\)M) in CH\(_2\)Cl\(_2\)-CH\(_3\)CN (1 : 1, v/v) containing 0.1 M Bu\(_4\)NPF\(_6\). Scan rate was 100 mV s\(^{-1}\).

11. The CT intensity

![The color changes of the CT complex gels of 3 (-Phe-Phe-) with increasing of TNP concentration in toluene.](image)

**Figure S9.** The color changes of the CT complex gels of 3 (-Phe-Phe-) with increasing of TNP concentration in toluene.
12. $T_{\text{gel}}$ of CT complex gels

Figure S10. The $T_{\text{gel}}$ of the CT complex gel (10 mg/mL) of 3 (-Phe-Phe-) in different period after addition in 2.0 eq. TNP in toluene.

13. The CV curves of CT complex gels

Figure S11. The CV curves of the CT complex xerogels in different period after addition of 2.0 eq. TNP from toluene: (a) native xerogel of 3 (-Phe-Phe-), incubated with TNP (b) 0 day, (c) 1 day, (d) 2 days, (e) 3 days, (f) 4 days and (g) 5 days.
14. The data from CV curves of CT complex gels

Table S3 The oxidation potentials of xerogels of TTF unit when incubated with 2.0 equiv. TNP in different times from toluene.

<table>
<thead>
<tr>
<th>Potential</th>
<th>Native gel</th>
<th>+ TNP 0 day</th>
<th>+ TNP 1 day</th>
<th>+ TNP 2 days</th>
<th>+ TNP 3 days</th>
<th>+ TNP 4 days</th>
<th>+ TNP 5 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ox}^1$ (V)</td>
<td>0.522</td>
<td>0.543</td>
<td>0.545</td>
<td>0.550</td>
<td>0.601</td>
<td>0.615</td>
<td>0.644</td>
</tr>
<tr>
<td>$E_{ox}^2$ (V)</td>
<td>0.833</td>
<td>0.831</td>
<td>0.838</td>
<td>0.850</td>
<td>0.871</td>
<td>0.898</td>
<td>0.946</td>
</tr>
</tbody>
</table>

15. Interaction with TNP on TLC strips

Figure S12. Photographs of 3-coated TLC strips after dipping into solutions of TNP in toluene (a) and water (b).

16. The reversible color changes of chemical redox

Figure S13. The color changes of 3 (-Phe-Phe-) in ethanol ($1 \times 10^{-4}$ M) solution by chemical redox.

17. Absorption of dyes by toluene gel
Figure S14. Photographs of an aqueous solution of Rhodamine B (a) and Crystal Violet (b) after adsorption by organogel 3 in toluene in different times; 1.0 mL of Crystal Violet or Rhodamine B \(2\times10^{-5}\) M was added on the top of 0.4 mL gel and the samples were tested at room temperature.

18. Structures of the dye molecules

![Scheme S1. The structures of the dye molecules.](image)

19. Absorption spectra of Methyl Orange and Indigo Carmine
**Figure S15.** The absorption spectra of aqueous solution of Methyl Orange (a) and Indigo Carmine (b) by absorption of cyclohexane gel of 3 in different times.