Supplementary Material (ESI) for *Soft Matter*

Supporting Information

Self- assembling tripeptide based hydrogels and their use in removal of dyes from waste-water

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Synthetic Procedure of Peptides.

Peptides 1-5 were synthesized by conventional solution phase methodology by using racemization free fragment condensation strategy.[S1] The N-terminus was protected by the Boc- group and C-terminus was protected as a methyl ester. Couplings were mediated by dicyclohexyl carbodiimide/ 1-hydroxybenzotriazole. Deprotection of the methyl ester was performed using the saponification method. All final compounds were fully characterized by mass spectrometry, ^{1}H-NMR spectroscopy (300 MH_Z) and ^{13}C-NMR spectroscopy (75 MH_Z).

1. Synthesis of Peptide (Boc-Leu-Phe-Phe-OH)

(i) Synthesis of Boc-Leu-OH: The synthesis of this compound was previously reported by our group.[S2]

(ii) Boc-Leu(1)-Phe(2)-OMe: 3.39 g (17 mmol) of Boc-Leu-OH was dissolved in 10 mL of dry DMF in an ice-water bath. H-Phe-OMe was isolated from 7.33 g (34 mmol) of the corresponding methyl ester hydrochloride by neutralization; subsequent extraction with ethyl acetate and ethyl acetate extract was concentrated to 10 mL. It was then added to the reaction mixture, followed immediately by 3.5 g (17 mmol) of dicyclohexyl carbodiimide (DCC) and 2.30 g (17 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and stirred for 3 days. The residue was taken up in ethyl acetate (40 mL) and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 1 M HCl (3 × 30 mL), brine (2 × 30 mL), 1M sodium carbonate (3 × 30 mL) and brine (2 × 30 mL) respectively. This washed organic solution was dried over anhydrous sodium sulfate and evaporated in vacuum. A white material was obtained. Yield: 5.70 g (14.52 mmol, 85.46 %).

^{1}H NMR (300 MHz, $CDCl_3$, 25º C, TMS): δ 7.31–7.21 (m, 5H, aromatic CH), δ 7.10 (d, ^{3}J(H, H) = 6.3 Hz, 1H, NH), δ 6.49 (d, ^{3}J(H, H) = 7.5 Hz, 1H, NH), δ 4.87–4.81 (m, 1H, αCH), δ 4.13–4.08 (m, 1H, αCH), δ 3.71 (s, 3H, –OCH_3), δ 3.19–3.04 (m, 2H, β CH_2), δ 1.69–1.56 (m, 3H, $\beta$$CH_2$ and γCH), δ 1.43 (s, 9H, Boc–CH_3), δ 0.92–0.89 (m, 6H, δ CH_3); Anal. Calcd. for $C_{21}H_{32}N_2O_5$ (392.49): C, 64.26; H, 8.22; N, 20.38%. Found C, 64.20; H, 8.20; N, 20.36%. MS (ESI) m/z 415.13 $(M+Na)^+$, 416.11$(M+Na+H)^+$; ^{13}C NMR (75 MHz, $CDCl_3$, 25º C): δ 172.28 (C of CO), δ 171.71 (C of CO), δ 155.52 (C of CO), δ 135.80 (one phenyl ring C attached with CH_2), δ 130.66 (2C, *m*-C of phenyl ring), δ 128.54 (2C, *o*-C of phenyl ring), δ 127.76 (*p*-C of phenyl ring), δ 80.06 (tertiary C of Boc), δ77.51-76.66 (C of $CDCl_3$), δ 53.18 (2C, αC), δ 52.29 (C of OCH_3), δ 41.23 (C of β CH_2), δ 37.92 (C of β CH_2), δ 28.29 (3C, primary C of Boc), δ 22.88 (2C, C of δ CH_3), δ 21.94 (C of γ CH).

(iii) Boc-Leu(1)-Phe(2)-OH: To 4.7 g (12 mmol) of Boc-Leu(1)-Phe(2)-OMe were added 25 mL MeOH and 15 mL of 1(M) NaOH and the progress of saponification was monitored by thin-layer chromatography (TLC). The reaction mixture was stirred. After 10 h, methanol was removed under vacuum and the residue was taken in 50 mL of water and washed with diethyl ether (2 × 50 mL). The pH of the aqueous layer was then adjusted to 2-3 using 1(N) HCl, the

aqueous layer was extracted with ethyl acetate (2 × 50 mL). The extract were pooled, dried over anhydrous sodium sulfate and evaporated in vacuum. Yield: 4.16 g (10.99 mmol, 91.63 %).

^{1}H NMR (300 MHz, DMSO-d_6, 25° C): δ 12.70 (br, 1H, –COOH), δ 7.90 (d, ^3J(H, H) = 7.5 Hz, 1H, NH) δ 7.25–7.21 (m, 5H, aromatic CH), δ 6.85 (d, ^3J(H, H) = 8.4 Hz, 1H, NH), δ 4.45–4.43 (m, 1H, α CH), δ 3.98–3.94 (m, 1H, α CH), δ 3.08–3.02 (m, 1H, β CH_2), δ 2.94–2.87 (m, 1H, β CH_2), 1.51–1.49 (m, 3H, β CH_2 and γ CH), δ 1.36 (s, 9H, Boc–CH_3), δ 0.85–0.76 (m, 6H, δ CH_3); Anal. Calcd. for $C_{20}H_{30}N_2O_5$ (378.46): C, 63.46; H, 7.99; N, 7.40%. Found C, 63.45; H, 8.01; N, 7.42%. MS (ESI) m/z 401.13 $(M+Na)^+$, 402.12 $(M+Na+H)^+$; ^{13}C NMR (75 MHz, DMSO-d_6, 25° C): δ 172.81 (C of COOH), δ 172.38 (C of CONH), δ 155.15 (C of CONH), δ 137.37 (one phenyl ring C attached with CH_2), δ 129.21 (2C, *m*-C of phenyl ring), δ 128.12 (2C, *o*-C of phenyl ring), δ 126.39 (*p*-C of phenyl ring), δ 78.03 (tertiary C of Boc), δ 53.08 (2C, α C), δ 52.58 (C of OCH_3), δ 40.58–36.78 (C of DMSO-d_6 and two β C), δ 28.19 (3C, primary C of Boc), δ 22.92 (C of δ CH_3), δ 21.59 (C of γ CH).

(iv) Boc-Leu(1)-Phe(2)-Phe(3)-OMe: 3.78 g (10 mmol) of Boc-Leu-Phe-OH was dissolved in 10 mL of dry DMF in an ice-water bath. H-Phe-OMe was isolated from 3.23 g (15 mmol) of the corresponding methyl ester hydrochloride by neutralization; subsequent extraction with ethyl acetate and ethyl acetate extract was concentrated to 10 mL. It was then added to the reaction mixture, followed immediately by 2.06 g (10 mmol) of dicyclohexyl carbodiimide (DCC) and 1.35 g (10 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and stirred for 3 days. The residue was taken up in ethyl acetate (40 mL) and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 1(N) HCl (3 × 30 mL), brine (2 × 30 mL), 1(M) sodium carbonate (3 × 30 mL) and brine (2 × 30 mL), dried over anhydrous sodium sulfate and evaporated in vacuum. A white material was obtained. Yield: 4.04 g (7.48 mmol, 74.95 %).

^{1}H NMR (300 MHz, $CDCl_3$, 25° C, TMS): δ 7.29–7.11 (m, 8H, aromatic CH), δ 6.99–6.98 (m, 2H, aromatic CH), δ 6.66 (d, ^3J (H, H)=7.8 Hz, 1H, NH), δ 6.31 (d, ^3J(H, H) = 8.3 Hz, 1H, NH), δ 4.831 (d, ^3J(H, H) = 7.5 Hz, 1H, NH), δ 4.76–4.09 (m, 1H, α CH), δ 4.66–4.59 (m, 1H, α CH), δ 4.05 (br, 1H, α CH), δ 3.66 (s, 3H, –OCH_3), δ 3.11–2.94 (m, 4H, β CH_2), δ 1.63–1.50 (m, 3H, β CH_2 and γ CH), δ 1.42 (s, 9H, Boc–CH_3), δ 0.89 (d, ^3J(H, H) = 6 Hz, 6H, δ CH_3); Anal. Calcd. for $C_{30}H_{41}N_3O_6$ (539.66): C, 66.77; H, 7.66; N, 7.79%. Found C, 66.78; H, 7.64; N, 7.80%. MS (ESI) m/z 562.05 $(M+Na)^+$, 563.08 $(M+Na+H)^+$, 578.06 $(M+K)^+$, 579.07 $(M+K+H)^+$; ^{13}C NMR (75 MHz, $CDCl_3$, 25° C): δ 172.53 (C of CO), δ 171.34 (C of CO), δ 170.24 (C of CO), δ 155.74 (C of CO), δ 136.46 (one phenyl ring C attached with CH_2), δ 135.76 (one phenyl ring C attached with CH_2), δ 129.52 (2C, *m*-C of phenyl ring), δ 129.28 (2C, *m*-C of phenyl ring), δ 128.77 (2C, *o*-C of phenyl ring), δ 128.70 (2C, *o*-C of phenyl ring), δ 127.25 (*p*-C of phenyl ring), δ 127.17 (*p*-C of phenyl ring), δ 77.58 (tertiary C of Boc), δ77.16-76.74 (C of $CDCl_3$), δ 54.30 (α C), δ 53.59 (2C, α C),

δ 52.39 (C of OCH_3), δ 41.23 (C of β CH_2), δ 38.18 (C of β CH_2), δ 37.97 (C of β CH_2), δ 28.42 (3C, primary C of Boc), δ 24.84 (C of δ CH_3), δ 24.44 (C of δ CH_3), δ 21.94 (C of γ CH).

(v) Boc-Leu(1)-Phe(2)-Phe(3)-OH: To 3.25 g (6 mmol) of Boc-Leu(1)-Phe(2)-Phe(3)-OMe were added 20 mL MeOH and 8 mL of 1(M) NaOH and the progress of saponification was monitored by thin-layer chromatography (TLC). The reaction mixture was stirred. After 10 h, methanol was removed under vacuum and the residue was taken in 50 mL of water and washed with diethyl ether (2x50 mL). The pH of the aqueous layer was then adjusted to 2-3 using 1(N) HCl, the aqueous layer was extracted with ethyl acetate (2x50 mL). The extract were pooled, dried over anhydrous sodium sulfate and evaporated in vacuum. Yield: 2.76 g (5.25 mmol, 87.62 %).

^{1}H NMR (300 MHz, DMSO-d_6, 25º C): δ 12.70 (br, 1H, –COOH), δ 8.35 (d, ^3J(H, H) = 7.5 Hz, 1H, NH), δ 7.69 (d, ^3J(H, H) = 8.1 Hz, 1H, NH), δ 7.30–7.15 (m, 10H, aromatic CH), δ 6.88 (d, ^3J(H, H) = 8.4 Hz, 1H, NH), δ 4.58–4.56 (m, 1H, α CH), δ 4.45–4.43 (m, 1H, α CH), δ 3.90–3.83 (m, 1H, α CH), δ 3.09–2.71 (m, 4H, β CH_2), δ 1.35 (s, 9H, Boc–CH_3), δ 1.30–1.15 (m, 3H, β CH_2 and γ CH) δ 0.82–0.76 (m, 6H, δ CH_3); $[\alpha]^{26}{}_D$ – 14.45 (*c* 1.43, CH_3OH); Anal. Calcd. for $C_{29}H_{39}N_3O_6$ (525.64): C, 66.26; H, 7.48; N, 7.99%. Found C, 66.24; H, 7.50; N, 8.04%. MS (ESI) m/z 548.08 $(M+Na)^+$, 549.11$(M+Na+H)^+$, 564.09 $(M+K)^+$, 565.11 $(M+K+H)^+$; ^{13}C NMR (75 MHz, DMSO-d_6, 25º C): δ 172.68 (C of COOH), δ 172.03 (C of CONH), δ 170.97 (C of CONH), δ 155.13 (C of CONH), δ 137.45 (one phenyl ring C attached with CH_2), δ 137.30 (one phenyl ring C attached with CH_2), δ 129.37 (2C, *m*-C of phenyl ring), δ 129.07 (2C, *m*-C of phenyl ring), δ 128.24 (2C, *o*-C of phenyl ring), δ 127.90 (2C, *o*-C of phenyl ring), δ 126.49 (*p*-C of phenyl ring), δ 126.19 (*p*-C of phenyl ring), δ 78.15 (tertiary C of Boc), δ 53.45 (α C), δ 53.03 (2C, α C), δ 40.97–36.73 (C of DMSO-d_6 and three β C), δ 28.18 (3C, primary C of Boc), δ 24.17 (C of γ CH), δ 22.90 (C of δ CH_3), δ 21.53 (C of δ CH_3).

2. Peptide (Boc -Phe-Phe-Leu -OH)

(i) Synthesis of Boc-Phe-OH: The synthesis of this compound was previously reported by our group.[S3]

(ii) Boc- Phe(1)-Phe(2)-OMe: 4.51 g (17 mmol) of Boc-Phe-OH was dissolved in 10 mL of dry DMF in an ice-water bath. H-Phe-OMe was isolated from 7.33 g (34 mmol) of the corresponding methyl ester hydrochloride by neutralization; subsequent extraction with ethyl acetate and ethyl acetate extract was concentrated to 10 mL. It was then added to the reaction mixture, followed immediately by 3.50 g (17 mmol) of dicyclohexyl carbodiimide (DCC) and 2.29 g (17 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and stirred for 3 days. The residue was taken up in ethyl acetate (40 mL) and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 1(N) HCl (3 × 30 mL), brine (2 × 30 mL), 1(M) sodium carbonate (3 × 30 mL) and brine (2 × 30 mL), dried over anhydrous sodium sulfate and evaporated in vacuum. A white material was obtained. Yield: 5.70 g (13.36 mmol, 78.62 %).

^{1}H NMR (300 MHz, $CDCl_3$, 25º C, TMS): δ 7.31–7.18 (m, 8H, aromatic CH), δ 6.99–6.97 (m, 2H, aromatic CH), δ 6.28 (d, ^3J(H, H) = 6.6 Hz, 1H, NH), δ 4.93 (d, ^3J(H, H) = 7.0 Hz, 1H, NH), δ 4.81–4.75 (m, 1H, α CH), δ 4.34–4.32 (m, 1H, α CH), δ 3.67 (s, 3H, $-OCH_3$), δ 3.11–2.98 (m, 4H, β CH_2), δ 1.40 (s, 9H, Boc–CH_3); Anal. Calcd. for $C_{24}H_{30}N_2O_5$ (426.51): C, 67.59; H, 7.09; N, 6.57%. Found C, 67.61; H, 7.1; N, 6.54%. MS (ESI) m/z 449.30 $(M+Na)^+$, 450.30 $(M+Na+H)^+$, 465.28 $(M+K)^+$; ^{13}C NMR (75 MHz, $CDCl_3$, 25° C): δ 171.46 (C of CO), δ 170.97 (C of CO), δ 155.35 (C of CO), δ 136.53 (one phenyl ring C attached with CH_2), δ 135.71 (one phenyl ring C attached with CH_2), δ 129.37 (2C, *m*-C of phenyl ring), δ 129.26 (2C, *m*-C of phenyl ring), δ 128.63 (2C, *o*-C of phenyl ring), δ 128.54 (2C, *o*-C of phenyl ring), δ 127.11 (*p*-C of phenyl ring), δ 126.94 (*p*-C of phenyl ring), δ 80.24 (tertiary C of Boc), δ77.52–76.67 (C of $CDCl_3$), δ 55.67 (C, αC), δ 53.31 (C, αC), δ 52.28 (C of OCH_3), δ 38.30 (C of β CH_2), δ 37.94 (C of β CH_2), δ 28.23 (3C, primary C of Boc).

(iii) Boc-Phe(1)-Phe(2)-OH: To 5.53 g (13 mmol) of Boc-Phe(1)-Phe(2)-OMe were added 25 mL MeOH and 15 mL of 1(M) NaOH and the progress of saponification was monitored by thin-layer chromatography (TLC). The reaction mixture was stirred. After 10 h, methanol was removed under vacuum and the residue was taken in 50 mL of water and washed with diethyl ether (2 × 50 mL). The pH of the aqueous layer was then adjusted to 2-3 using 1(N) HCl, the aqueous layer was extracted with ethyl acetate (2 × 50 mL). The extract were pooled, dried over anhydrous sodium sulfate and evaporated in vacuum. Yield: 4.94 g (11.98 mmol, 92.16 %).

^{1}H NMR (300 MHz, DMSO-d_6, 25º C): δ 8.06 (d, ^3J(H, H) = 9 Hz, 1H, NH), δ 7.29–7.15 (m, 10H, aromatic CH), δ 6.9 (d, ^3J(H, H) = 9 Hz, 1H, NH), δ 4.47–4.40 (m, 1H, αCH), δ 4.18–4.11 (m, 1H, αCH), δ 3.12–3.06 (m, 2H, β CH_2), δ 2.98–2.88 (m, 2H, β CH_2), δ 1.28 (s, 9H, Boc–CH_3); Anal. Calcd. for $C_{23}H_{28}N_2O_5$ (412.48): C, 66.97; H, 6.84; N, 6.97%. Found C, 67.00; H, 6.86; N, 6.91%. MS (ESI) m/z 435.33 $(M+Na)^+$, 436.34 $(M+Na+H)^+$, 451.30 $(M+K)^+$; ^{13}C NMR (75 MHz, DMSO-d_6, 25° C): δ 173.34 (C of COOH), δ 172.23 (C of CONH), δ 155.65 (C of CONH), δ 138.65 (one phenyl ring C attached with CH_2), δ 137.88 (one phenyl ring C attached with CH_2), δ 129.78 (2C, *m*-C of phenyl ring), δ 129.73 (2C, *m*-C of phenyl ring), δ 128.74 (2C, *o*-C of phenyl ring), δ 128.53 (2C, *o*-C of phenyl ring), δ 127.01 (*p*-C of phenyl ring), δ 126.69 (*p*-C of phenyl ring), δ 78.59 (tertiary C of Boc), δ 56.24 (αC), δ 53.88 (αC), δ δ 40.86–39.19 (C of DMSO-d_6), δ 38.01 (C of β CH_2), δ 37.36 (C of β CH_2), δ 28.66 (3C, primary C of Boc).

(iv) Boc-Phe(1)-Phe(2)-Leu(3)-OMe: 4.53 g (11 mmol) of Boc-Phe-Phe-OH was dissolved in 10 mL of dry DMF in an ice-water bath. H-Leu-OMe was isolated from 2.99 g (16.5 mmol) of the corresponding methyl ester hydrochloride by neutralization; subsequent extraction with ethyl acetate and ethyl acetate extract was concentrated to 10 mL. It was then added to the reaction mixture, followed immediately by 2.27 g (10 mmol) of dicyclohexyl carbodiimide (DCC)

and 1.49 g (10 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and stirred for 3 days. The residue was taken up in ethyl acetate (40 mL) and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 1(N) HCl (3 × 30 mL), brine (2 × 30 mL), 1(M) sodium carbonate (3 × 30 mL) and brine (2 × 30 mL), dried over anhydrous sodium sulfate and evaporated in vacuum. A white material was obtained. Yield: 4.85 g (8.99 mmol, 81.65 %).

^{1}H NMR (300 MHz, $CDCl_3$, 25° C, TMS): δ 7.34–7.07 (m, 10H, aromatic CH), δ 6.46 (d, ^3J(H, H) = 6 Hz, 1H, NH), δ 6.29 (br, 1H, NH), δ 4.82 (d, ^3J(H, H) = 6.6 Hz, 1H, NH), δ 4.65–4.63 (m, 1H, α CH), 4.51–4.48 (m, 1H, α CH), δ 4.31–4.29 (m, 1H, α CH), δ 3.70 (s, 3H, $-OCH_3$), δ 3.14–2.88 (m, 4H, β CH_2), δ 1.59–1.45 (m, 3H, β CH_2 and γ CH), δ 1.34 (s, 9H, Boc–CH_3), δ 0.90–0.87 (m, 6H, δ CH_3); Anal. Calcd. for $C_{30}H_{41}N_3O_6$ (539.66): C, 66.77; H, 7.66; N, 7.79%. Found C, 66.82; H, 7.68; N, 7.75%. MS (ESI) m/z 562.35 $(M+Na)^+$, 563.37$(M+Na+H)^+$; ^{13}C NMR (75 MHz, $CDCl_3$, 25° C): δ 172.73 (C of CO), δ 171.19 (C of CO), δ 170.28 (C of CO), δ 155.74 (C of CO), δ 136.39 (one phenyl ring C attached with CH_2), δ 136.36 (one phenyl ring C attached with CH_2), δ 129.50 (2C, *m*-C of phenyl ring), δ 129.40 (2C, *m*-C of phenyl ring), δ 128.95 (2C, *o*-C of phenyl ring), δ 128.80 (2C, *o*-C of phenyl ring), δ 127.31 (*p*-C of phenyl ring), δ 127.22 (*p*-C of phenyl ring), δ 77.58 (tertiary C of Boc), δ77.36–75.73 (C of $CDCl_3$), δ 55.95 (C, α C), δ 54.21 (C, α C), δ 52.39 (C of OCH_3), δ 51.07 (C, α C), δ 41.36 (C of β CH_2), δ 37.99 (2C of β CH_2), δ 28.31 (3C, primary C of Boc), δ 24.76 (C of γ CH), δ 22.84 (C of δ CH_3), δ 21.98 (C of δ CH_3).

(v) Boc-Phe(1)-Phe(2)-Leu(3)-OH: To 3.25 g (6 mmol) of Boc-Phe(1)-Phe(2)-Leu(3)-OMe were added 20 mL MeOH and 8 mL of 1(M) NaOH and the progress of saponification was monitored by thin-layer chromatography (TLC). The reaction mixture was stirred. After 10 h, methanol was removed under vacuum and the residue was taken in 50 mL of water and washed with diethyl ether (2x50 mL). The pH of the aqueous layer was then adjusted to 2-3 using 1(N) HCl, the aqueous layer was extracted with ethyl acetate (2x50 mL). The extract were pooled, dried over anhydrous sodium sulfate and evaporated in vacuum. Yield: 2.76 g (5.25 mmol, 87.62 %).

^{1}H NMR (300 MHz, DMSO-d_6, 25° C): δ 12.57 (br, 1H, –COOH), δ 8.30 (d, ^3J(H, H) = 7.89 Hz, 1H, NH), δ 7.91 (d, ^3J(H, H) = 8.25 Hz, 1H, NH), δ 7.27–7.18 (m, 10H, aromatic CH), δ 6.87 (d, ^3J(H, H) = 8.55 Hz, 1H, NH), δ 4.62–4.60 (m, 1H, α CH), δ 4.30–4.22 (m, 1H, α CH), δ 4.09 (br, 1H, α CH), δ 3.09–3.03 (m, 1H, β CH_2), δ 2.86–2.78 (m, 2H, β CH_2), δ 2.68–2.60 (m, 1H, β CH_2), δ 1.64–1.52 (m, 3H, β CH_2 and γ CH), δ 1.28 (s, 9H, Boc–CH_3), δ 0.92–0.84 (m, 6H, δ CH_3); $[\alpha]^{26}_{D}$ – 23.11 (*c* 1.01, CH_3OH); Anal. Calcd. for $C_{29}H_{39}N_3O_6$ (525.64): C, 66.26; H, 7.48; N, 7.99%. Found C, 66.30; H, 7.50; N, 7.95%. MS (ESI) m/z 548.28 $(M+Na)^+$, 549.29 $(M+Na+H)^+$, 564.26 $(M+K)^+$; ^{13}C NMR (75 MHz, DMSO-d_6, 25° C): δ 174.69 (C of COOH), δ 172.12 (C of CONH), δ 171.74 (C of CONH), δ 155.86 (C of CONH), δ 138.94 (one phenyl ring C attached with CH_2), δ 138.93 (one phenyl ring C attached with CH_2), δ 130.25

(2C, *m*-C of phenyl ring), δ 129.96 (2C, *m*-C of phenyl ring), δ 128.82 (4C, *o*-C of phenyl ring), δ 127.09 (*p*-C of phenyl ring), δ 126.98 (*p*-C of phenyl ring), δ 78.98 (tertiary C of Boc), δ 56.77 (αC), δ 54.10 (αC), δ 51.08 (αC), δ 41.22–38.34 (C of DMSO-d_6 and three β C), δ 28.94 (3C, primary C of Boc), δ 25.12 (C of γ CH), δ 23.70 (C of δ CH_3), δ 22.17 (C of δ CH_3).

3. Peptide (Boc-Leu-Phe-Leu -OH)

(i) Synthesis of Boc-Leu-Phe-OH: This compound has been prepared according to the above mentioned procedure for the synthesis of peptide **1**.

(ii) Boc-Leu(1)-Phe(2)-Leu(3)-OMe: 3.78 g (10 mmol) of Boc-Leu-Phe-OH was dissolved in 10 mL of dry DMF in an ice-water bath. H-Leu-OMe was isolated from 2.72 g (15 mmol) of the corresponding methyl ester hydrochloride by neutralization; subsequent extraction with ethyl acetate and ethyl acetate extract was concentrated to 10 mL. It was then added to the reaction mixture, followed immediately by 3.09 g (10 mmol) of dicyclohexyl carbodiimide (DCC) and 2.02 g (10 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and stirred for 3 days. The residue was taken up in ethyl acetate (40 mL) and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 1(N) HCl (3 × 30 mL), brine (2 × 30 mL), 1(M) sodium carbonate (3 × 30 mL) and brine (2 × 30 mL), dried over anhydrous sodium sulfate and evaporated in vacuum. A white material was obtained. Yield: 3.84 g (7.59 mmol, 75.89%)

^{1}H NMR (300 MHz, $CDCl_3$, 25° C, TMS): δ 7.31–7.16 (m, 5H, aromatic CH), δ 6.69 (d, ^3J(H, H)=7.2 Hz 1H, NH), δ 6.44 (br, 1H, NH), δ 4.81 (d, ^3J(H, H) = 6.6 Hz, 1H, NH), δ 4.72–4.65 (m, 1H, αCH), 4.52–4.50 (m, 1H, αCH), δ 4.05 (br, 1H, αCH), δ 3.69 (s, 3H, –OCH_3), δ 3.14–3.01 (m, 2H, β CH_2), δ 1.61–1.46 (m, 6H, β CH_2 and γ CH), δ 1.40 (s, 9H, Boc–CH_3), δ 0.90–0.86 (m, 12H, δ CH_3); Anal. Calcd. for $C_{27}H_{43}N_3O_6$ (505.65): C, 64.13; H, 8.57; N, 8.31%. Found C, 64.15; H, 8.6; N, 8.29%. MS (ESI) m/z 528.14 $(M+Na)^+$, 529.16 $(M+Na+H)^+$; ^{13}C NMR (75 MHz, $CDCl_3$, 25° C): δ 172.71 (C of CO), δ 171.69 (C of CO), δ 171.60 (C of CO), δ 155.77 (C of CO), δ 135.84 (one phenyl ring C attached with CH_2), δ 129.25 (2C, *m*-C of phenyl ring), δ 128.55 (2C, *o*-C of phenyl ring), δ 127.08 (C of phenyl ring), δ 80.04 (tertiary C of Boc), δ77.53–76.68 (C of $CDCl_3$), δ 53.38 (αC), δ 52.97 (αC), δ 52.22 (C of OCH_3), δ 51.69 (α C), δ 41.05 (C of β CH_2), δ 40.84 (C of β CH_2), δ 37.91 (C of β CH_2), δ 29.39 (3C, primary C of Boc), δ 24.63 (2C, C of δ CH_3), δ 24.58 (2C, C of δ CH_3), δ 22.99 (C of γ CH), δ 22.86 (C of γ CH).

(iii) Boc-Leu(1)-Phe(2)-Leu(3)-OH: To 3.35 g (7 mmol) of Boc-Leu(1)-Phe(2)-Leu(3)-OMe were added 20 mL MeOH and 8 mL of 1(M) NaOH and the progress of saponification was monitored by thin-layer chromatography (TLC). The reaction mixture was stirred. After 10 h, methanol was removed under vacuum and the residue was taken in 50 mL of water and washed with diethyl ether (2x50 mL). The pH of the aqueous layer was then adjusted to 2-3 using 1(N) HCl,

the aqueous layer was extracted with ethyl acetate (2x50 mL). The extract were pooled, dried over anhydrous sodium sulfate and evaporated in vacuum. Yield: 2.95 g (6 mmol, 85.76%).

^{1}H NMR (300 MHz, DMSO-d_6, 25° C): δ 12.56 (br, 1H, –COOH), δ 8.26 (d, ^3J(H, H) = 7.7 Hz, 1H, NH), δ 7.72 (d, ^3J(H, H) = 8.18 Hz, 1H, NH), δ 7.21–7.16 (m, 5H, aromatic CH), δ 6.91 (d, ^3J(H, H)=8.29 Hz, 1H, NH), δ 4.59–4.58 (m, 1H, α CH), δ 4.25–4.23 (m, 1H, α CH), δ 3.88–3.86 (br, 1H, α CH), δ 3.05–2.99 (m, 1H, β CH_2), δ 2.82–2.75 (m, 1H, β CH_2), δ 1.55–1.50 (m, 4H, β CH_2), δ 1.36 (s, 9H, Boc–CH_3), δ 1.30–1.25 (m, 2H, γ CH), δ 0.90–0.72 (m, 12H, δ CH_3); $[\alpha]^{26}{}_D$ – 33.81 (*c* 1.17, CH_3OH); Anal. Calcd. for $C_{26}H_{41}N_3O_6$ (491.62): C, 63.52; H, 8.41; N, 8.55%. Found C, 63.50; H, 8.44; N, 8.53%. MS (ESI) m/z 514.39 $(M+Na)^+$, 515.37 $(M+Na+H)^+$, 530.35 $(M+K)^+$; ^{13}C NMR (75 MHz, DMSO-d_6, 25° C): δ 174.654 (C of COOH), δ 172.92 (C of CONH), δ 171.71 (C of CONH), δ 155.97 (C of CONH), δ 138.29 (one phenyl ring C attached with CH_2), δ 130.20 (2C, *m*-C of phenyl ring), δ 128.72 (2C, *o*-C of phenyl ring), δ 126.99 (*p*-C of phenyl ring), δ 78.94 (tertiary C of Boc), δ 53.99 (α C), δ 53.78 (α C), δ 51.05 (α C), δ 41.75–38.55 (C of DMSO-d_6 and three β C), δ 29.03 (3C, primary C of Boc), δ 25.07 (C of γ CH), δ 25.01 (C of γ CH), δ 23.69 (2C, C of δ CH_3), δ 22.14 (2C, C of δ CH_3).

4. Synthesis of Peptide (Boc-Val-Phe-Phe-OH)

(i) Synthesis of Boc-Val-OH: A solution of L-Valine (2.34 g, 20 mmol) in a mixture of dioxane (40mL), water (20mL) and 1M NaOH (20mL) was stirred and cooled in an ice water bath. Di-tert-butyl pyrocarbonate (4.8 g, 22 mmol) was added and stirring was continued at room temperature for 6 h. Then the solution was concentrated in vacuum to about 20-25 mL, cooled in an ice water bath, covered with a layer of ethyl acetate (about 20 mL), and acidified with a dilute solution of $KHSO_4$ to pH 2-3 (congo red). The aqueous phase was extracted with ethyl acetate and this operation was done repeatedly. The ethyl acetate extract were pooled, washed with water, dried over anhydrous Na_2SO_4 and evaporated in vacuum. The pure material was obtained as a waxy solid.

Yield: 3.95 g (18.2 mmol, 91%); Anal. Calcd. for $C_{10}H_{19}NO_4$ (217.26): C, 55.28; H, 8.81; N, 6.45%. Found C, 55.30; H, 8.85; N, 6.40%.

(ii) Boc-Val(1)-Phe(2)-OMe: 3.69 g (17mmol) of Boc-Val-OH was dissolved in 10 mL of dry DMF in an ice-water bath. H-Phe-OMe was isolated from 7.33 g (34 mmol) of the corresponding methyl ester hydrochloride by neutralization; subsequent extraction with ethyl acetate and ethyl acetate extract was concentrated to 10 mL. It was then added to the reaction mixture, followed immediately by 3.5 g (17 mmol) of dicyclohexyl carbodiimide (DCC) and 2.297 g (17 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and stirred for 3 days. The residue was taken up in ethyl acetate (40 mL) and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 1(N) HCl (3 × 30 mL), brine (2 × 30 mL), 1(M) sodium carbonate (3 × 30 mL) and brine (2 × 30 mL),

dried over anhydrous sodium sulfate and evaporated in vacuum. A white material was obtained. Yield: 5.29 g (13.98 mmol, 82.27 %).

^{1}H NMR (300 MHz, $CDCl_3$, 25° C, TMS): δ 7.32–7.22 (m, 3H, aromatic CH), δ 7.13–7.10 (m, 2H, aromatic CH), δ 6.35 (d, ^3J(H, H)=6.3 Hz, 1H, NH), δ 5.03(d, ^3J(H, H) = 7.5 Hz, 1H, NH), δ 4.90–4.84 (m, 1H, αCH), δ 3.93–3.88 (m, 1H, αCH), δ 3.73 (s, 3H, –OCH_3), δ 3.13–3.10 (m, 2H, β CH_2), δ 2.12–2.05 (m, 1H, β CH), δ 1.45 (s, 9H, Boc–CH_3), δ 0.93–0.86 (m, 6H, γCH_3); Anal. Calcd. for $C_{20}H_{30}N_2O_5$ (378.46): C, 63.47; H, 7.99; N, 7.40%. Found C, 63.51; H, 8.01; N, 7.35%. MS (ESI) m/z 401.05 $(M+Na)^+$, 402.03 $(M+Na+H)^+$, 417.02 $(M+K)^+$; ^{13}C NMR (75 MHz, $CDCl_3$, 25° C): δ 171.84 (C of CO), δ 171.28 (C of CO), δ 155.47 (C of CO), δ 136.68 (one phenyl ring C attached with CH_2), δ 129.34 (2C, *m*-C of phenyl ring), δ 128.62 (2C, *o*-C of phenyl ring), δ 126.88 (*p*-C of phenyl ring), δ 80.18 (tertiary C of Boc), δ77.52-76.67 (C of $CDCl_3$), δ 57.27 (C, αC), δ 55.82 (C, αC), δ 52.06 (C of OCH_3), δ 38.04 (C of β CH_2), δ 31.25 (C of β CH_2), δ 28.26 (3C, primary C of Boc), δ 18.83 (C of γ CH), δ 17.79 (C of γ CH).

(iii) Boc-Val(1)-Phe(2)-OH: To 4.54 g (12 mmol) of Boc-Val(1)-Phe(2)-OMe were added 25 mL MeOH and 15 mL of 1(M) NaOH and the progress of saponification was monitored by thin-layer chromatography (TLC). The reaction mixture was stirred. After 10 h, methanol was removed under vacuum and the residue was taken in 50 mL of water and washed with diethyl ether (2 × 50 mL). The pH of the aqueous layer was then adjusted to 2-3 using 1(N) HCl, the aqueous layer was extracted with ethyl acetate (2 × 50 mL). The extract were pooled, dried over anhydrous sodium sulfate and evaporated in vacuum. Yield: 4.19 g (11.50 mmol, 95.88%).

^{1}H NMR (300 MHz, DMSO-d_6, 25° C): δ12.62 (br, 1H, –COOH), δ 8.06 (*d,* ^3J(H, H) = 7.8 Hz, 1H, NH), δ 7.28–7.17 (m, 5H, aromatic CH), δ 6.59 (d, ^3J(H, H) = 9.3 Hz, 1H, NH), δ 4.48–4.40 (m, 1H, αCH), δ 3.78–3.73 (m, 1H, αCH), δ 3.08–3.02 (m, 1H, β CH_2), δ 2.92–2.84 (m, 1H, β CH_2), δ 1.87–1.81 (m, 1H, β CH), δ 1.37 (s, 9H, Boc–CH_3), δ 0.77–0.73 (m, 6H, γCH_3); Anal. Calcd. for $C_{19}H_{28}N_2O_5$ (364.44): C, 62.62; H, 7.74; N, 7.69%. Found C, 62.24; H, 7.78; N 7.66%. MS (ESI) m/z 387 $(M+Na)^+$, 403.01 $(M+K)^+$, 404.00 $(M+K+H)^+$; ^{13}C NMR (75 MHz, DMSO-d_6, 25° C): δ 173.36 (C of COOH), δ 172.39 (C of CONH), δ 155.72 (C of CONH), δ 138.64 (one phenyl ring C attached with CH_2), δ 129.68 (2C, *m*-C of phenyl ring), δ 128.45 (2C, *o*-C of phenyl ring), δ 126.63 (*p*-C of phenyl ring), δ 78.53 (tertiary C of Boc), δ 57.44 (αC), δ 56.10 (αC), δ 40.78–39.12 (C of DMSO-d_6), δ 37.69 (β C), δ 30.66 (β C), δ 28.57 (3C, primary C of Boc), δ 19.50 (C of γ CH_3), δ 18.33 (C of γ CH_3).

(iv) Boc-Val(1)-Phe(2)-Phe(3)-OMe: 3.64 g (10 mmol) of Boc-Val-Phe-OH was dissolved in 10 mL of dry DMF in an ice-water bath. H-Phe-OMe was isolated from 3.24 g (15 mmol) of the corresponding methyl ester hydrochloride by neutralization; subsequent extraction with ethyl acetate and ethyl acetate extract was concentrated to 10 mL. It was then added to the reaction mixture, followed immediately by 2.06 g (10 mmol) of dicyclohexyl carbodiimide (DCC)

and 1.35 g (10 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and stirred for 3 days. The residue was taken up in ethyl acetate (40 mL) and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 1(N) HCl (3 × 30 mL), brine (2 × 30 mL), 1(M) sodium carbonate (3 × 30 mL) and brine (2 × 30 mL), dried over anhydrous sodium sulfate and evaporated in vacuum. A white material was obtained. Yield: 4.20 g (8 mmol, 79.84 %).

^{1}H NMR (300 MHz, $CDCl_3$, 25° C, TMS): δ 7.29–7.18 (m, 8H, aromatic CH), δ 6.98–6.95 (m, 2H, aromatic CH), δ 6.60 (d, ^3J(H, H) = 7.8 Hz, 1H, NH), δ 6.33 (d, ^3J(H, H) = 7.9 Hz, 1H, NH), δ 5.00 (d, ^3J(H, H) = 8.1 Hz, 1H, NH), δ 4.76–4.65 (m, 2H, 2α CH), δ 3.94–3.89 (m, 1H, α CH), δ 3.64 (s, 3H, –OCH_3), δ 3.13–2.94 (m, 4H, β CH_2), δ 2.10–2.04 (m, 1H, β CH), δ 1.43 (s, 9H, Boc–CH_3), δ 0.88–0.78 (m, 6H, γ CH_3); Anal. Calcd. for $C_{29}H_{39}N_3O_6$ (525.64): C, 66.26; H, 7.48; N, 7.99%. Found C, 66.31; H, 7.50; N, 7.95%. MS (ESI) m/z 548.11 $(M+Na)^+$, 549.13$(M+Na+H)^+$, 564.10 $(M+K)^+$; ^{13}C NMR (75 MHz, $CDCl_3$, 25° C): δ 171.49 (C of CO), δ 171.19 (C of CO), δ 170.16 (C of CO), δ 155.78 (C of CO), δ 136.25 (one phenyl ring C attached with CH_2), δ 135.61 (one phenyl ring C attached with CH_2), δ 129.33 (2C, *m*-C of phenyl ring), δ 129.11 (2C, *m*-C of phenyl ring), δ 128.58 (2C, *o*-C of phenyl ring), δ 128.49 (2C, *o*-C of phenyl ring), δ 127.04 (*p*-C of phenyl ring), δ 126.96 (*p*-C of phenyl ring), δ 79.89 (tertiary C of Boc), δ77.45–76.61 (C of $CDCl_3$), δ 59.94 (C, αC), δ 54.10 (C, αC), δ 53.41 (C, αC), δ 52.18 (C of OCH_3), δ 38.24 (C of β CH_2), δ 37.85 (C of β CH_2), δ 30.71 (C of β CH_2), δ 28.27 (3C, primary C of Boc), δ 19.18 (C of γ CH_3), δ 17.49 (C of γ CH_3).

(v) Boc-Val(1)-Phe(2)-Phe(3)-OH: To 3.67 g (7 mmol) of Boc-Val(1)-Phe(2)-Phe(3)-OMe were added 20 mL MeOH and 8 mL of 1(M) NaOH and the progress of saponification was monitored by thin-layer chromatography (TLC). The reaction mixture was stirred. After 10 h, methanol was removed under vacuum and the residue was taken in 50 mL of water and washed with diethyl ether (2x50 mL). The pH of the aqueous layer was then adjusted to 2-3 using 1(N) HCl, the aqueous layer was extracted with ethyl acetate (2x50 mL). The extract were pooled, dried over anhydrous sodium sulfate and evaporated in vacuum. Yield: 3.22 g (6.29 mmol, 89.94 %).

^{1}H NMR (300 MHz, DMSO-d_6, 25° C): δ 12.50 (br, 1H, –COOH), δ 8.34 (d, ^3J(H, H) = 7.8 Hz, 1H, NH), δ 7.84 (d, ^3J(H, H) = 8.4 Hz, 1H, NH), δ 7.29–7.15 (m, 10H, aromatic CH), δ 6.62 (d, ^3J(H, H) = 9.3 Hz, 1H, NH), δ 4.64–4.61 (m, 1H, αCH), δ 4.52–4.41 (m, 1H, αCH), δ 3.73–3.67 (m, 1H, αCH), δ 3.11–2.88 (m, 3H, β CH_2), δ 2.77–2.69 (m, 1H, β CH_2), δ 1.79–1.73 (m, 1H, β CH), δ 1.37 (s, 9H, Boc–CH_3), δ 0.67–0.61 (m, 6H, γ CH_3); $[\alpha]^{26}{}_D$ – 18.03 (*c* 1.31, CH_3OH); Anal. Calcd. for $C_{28}H_{37}N_3O_6$ (511.61): C, 65.73; H, 7.29; N, 8.21%. Found C, 65.75; H, 7.33; N, 8.16%. MS (ESI) m/z 534.42 $(M+Na)^+$, 535.46$(M+Na+H)^+$; ^{13}C NMR (75 MHz, DMSO-d_6, 25° C): δ 172.54 (C of COOH), δ 171.02 (C of CONH), δ 170.85 (C of CONH), δ 155.20 (C of CONH), δ 137.54 (one phenyl ring C attached with CH_2), δ 137.24 (one phenyl ring C attached with CH_2), δ 129.19 (2C, *m*-C of phenyl ring), δ 129.01 (2C, *m*-C of phenyl ring),

δ 128.15 (2C, *o*-C of phenyl ring), δ 127.89 (2C, *o*-C of phenyl ring), δ 126.40 (*p*-C of phenyl ring), δ 126.13 (*p*-C of phenyl ring), δ 78.02 (tertiary C of Boc), δ 59.89 (αC), δ 53.35 (αC), δ 53.22 (αC), δ 40.33–38.66 (C of DMSO-d_6), δ 37.81 (βC), δ 36.72 (βC), δ 30.52 (βC), δ 28.12 (3C, primary C of Boc), δ 19.08 (C of γ CH_3), δ 17.99 (C of γ CH_3).

5. Synthesis of Peptide (Boc -Phe-Phe-Val -OH)

(i) Synthesis of Boc-Phe-Phe-OH: This compound has been prepared according to peptide **2**.

(ii) Boc-Phe(1)-Phe(2)-Val (3)-OMe: 4.53 g (11 mmol) of Boc-Phe-Phe-OH was dissolved in 10 mL of dry DMF in an ice-water bath. H-Val-OMe was isolated from 2.76 g (11.60 mmol) of the corresponding methyl ester hydrochloride by neutralization; subsequent extraction with ethyl acetate and ethyl acetate extract was concentrated to 10 mL. It was then added to the reaction mixture, followed immediately by 2.27 g (11 mmol) of dicyclohexyl carbodiimide (DCC) and 1.49 g (11 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and stirred for 3 days. The residue was taken up in ethyl acetate (40 mL) and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 1(N) HCl (3 × 30 mL), brine (2 × 30 mL), 1(M) sodium carbonate (3 × 30 mL) and brine (2 × 30 mL), dried over anhydrous sodium sulfate and evaporated in vacuum. A white material was obtained. Yield: 4.73 g (9 mmol, 81.83 %).

^{1}H NMR (300 MHz, $CDCl_3$, 25° C, TMS): δ7.31–7.09 (m, 10H, aromatic CH), δ6.58 (d, ^3J(H, H) = 7.2 Hz, 1H, NH), δ6.35 (d, ^3J(H, H) = 7.5 Hz, 1H, NH), δ4.91 (d, ^3J(H, H) = 5.4 Hz, 1H, NH), δ 4.68–4.61 (m, 1H, αCH), δ 4.42–4.34 (m, 2H, 2α CH), δ3.69 (s, 3H, –OCH_3), δ3.31–2.90 (m, 4H, β CH_2), δ2.10–2.01 (m, 1H, β CH), δ1.36 (s, 9H, Boc–CH_3), δ 0.86–0.74 (m, 6H, γCH_3); Anal. Calcd. for $C_{29}H_{39}N_3O_6$ (525.64): C, 66.26; H, 7.48; N, 7.99%. Found C, 66.28; H, 7.55; N, 8.04%. MS (ESI) m/z 548.30 $(M+Na)^+$, 549.31$(M+Na+H)^+$, 564.29 $(M+K)^+$; ^{13}C NMR (75 MHz, $CDCl_3$, 25° C): δ 171.57 (C of CO), δ 171.19 (C of CO), δ 170.28 (C of CO), δ 155.28 (C of CO), δ 136.37 (one phenyl ring C attached with CH_2), δ 136.25 (one phenyl ring C attached with CH_2), δ 129.31 (2C, *m*-C of phenyl ring), δ 129.28 (2C, *m*-C of phenyl ring), δ 128.76 (2C, *o*-C of phenyl ring), δ 128.68 (2C, *o*-C of phenyl ring), δ 127.09 (*p*-C of phenyl ring), δ 127.05 (*p*-C of phenyl ring), δ 80.44 (tertiary C of Boc), δ77.46–76.61 (C of $CDCl_3$), δ 57.49 (αC), δ 55.81 (αC), δ 54.48 (αC), δ 52.09 (C of OCH_3), δ 37.98 (2C, βC), δ 31.07 (βC), δ 28.21 (3C, primary C of Boc), δ 18.85 (C of γ CH_3), δ 17.87 (C of γ CH_3).

(iii) Boc-Phe(1)-Phe(2)-Val(3)-OH: To 3.68 g (7 mmol) of Boc-Phe(1)-Phe(2)-Val(3)-OMe were added 20 mL MeOH and 8 mL of 1(M) NaOH and the progress of saponification was monitored by thin-layer chromatography (TLC). The reaction mixture was stirred. After 10 h, methanol was removed under vacuum and the residue was taken in 50 mL of water and washed with diethyl ether (2x50 mL). The pH of the aqueous layer was then adjusted to 2-3 using 1(N) HCl,

the aqueous layer was extracted with ethyl acetate (2x50 mL). The extract were pooled, dried over anhydrous sodium sulfate and evaporated in vacuum. Yield: 3.06 g (5.98 mmol, 85.47%).

^{1}H NMR (300 MHz, DMSO-d_6, 25° C): δ 12.69 (br, 1H, –COOH), δ 8.19 (d, ^3J(H, H) = 9.6 Hz, 1H, NH), δ 7.95 (d, ^3J(H, H) = 8.4 Hz, 1H, NH), δ 7.27–7.07 (m, 10H, aromatic CH), δ 6.89 (d, ^3J(H, H) = 8.7 Hz, 1H, NH), δ 4.71–4.69 (m, 1H, α CH), δ 4.20–4.16 (m, 2H, 2α CH), δ 3.08–3.02 (m, 1H, β CH_2), δ 2.87–2.79 (m, 2H, β CH_2), δ 2.68–2.63 (m, 1H, β CH_2), δ 2.09–2.05 (m, 1H, β CH), δ 1.27 (s, 9H, Boc–CH_3), δ 0.91–0.83 (m, 6H, γ CH_3); $[\alpha]^{26}{}_D$ – 16.66 (*c* 0.89, CH_3OH); Anal. Calcd. for $C_{28}H_{37}N_3O_6$ (511.61): C, 65.73; H, 7.29; N, 8.21. Found C, 65.76; H, 7.35; N, 8.15. MS (ESI) m/z 534.36 $(M+Na)^+$, 535.38 $(M+Na+H)^+$, 550.36 $(M+K)^+$; ^{13}C NMR (75 MHz, DMSO-d_6, 25° C): δ 172.91 (C of COOH), δ 171.49 (C of CONH), δ 171.25 (C of CONH), δ 155.11 (C of CONH), δ 138.15 (one phenyl ring C attached with CH_2), δ 137.55 (one phenyl ring C attached with CH_2), δ 129.48 (2C, *m*-C of phenyl ring), δ 129.20 (2C, *m*-C of phenyl ring), δ 128.06 (4C, *o*-C of phenyl ring), δ 126.35 (*p*-C of phenyl ring), δ 126.23 (*p*-C of phenyl ring), δ 78.21 (tertiary C of Boc), δ 57.24 (α C), δ 56.00 (α C), δ 53.32 (α C), δ 40.34–38.67 (C of DMSO-d_6), δ 37.77 (β C), δ 37.57 (β C), δ 30.01 (β C), δ 28.16 (3C, primary C of Boc), δ 19.18 (C of γ CH_3), δ 18.01 (C of γ CH_3).

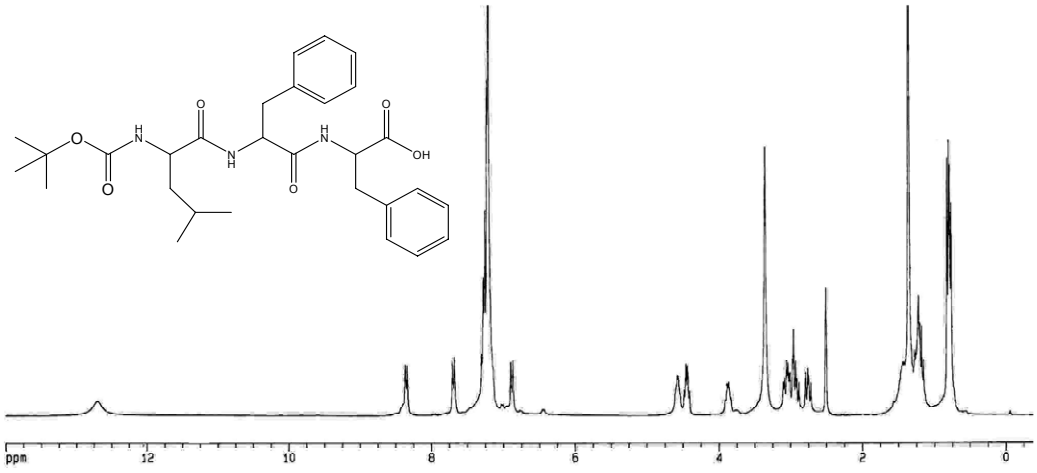


Figure S1: 300 MHz NMR Spectrum of Peptide **1**

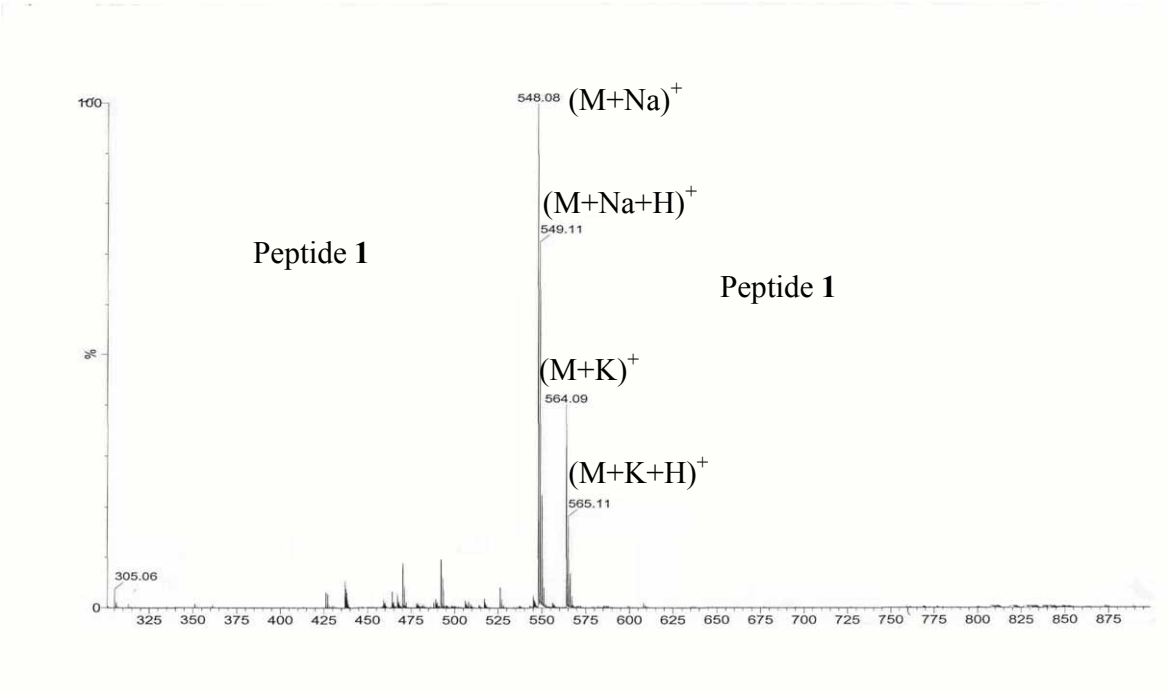


Figure S2: ESI-MS Spectrum of Peptide **1**

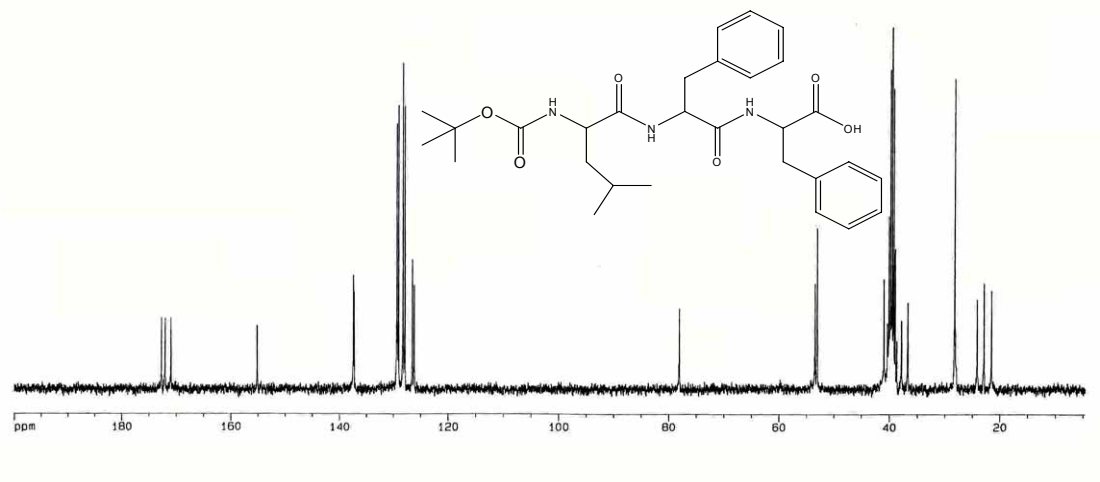


Figure S3: ^{13}C NMR Spectrum of Peptide **1**

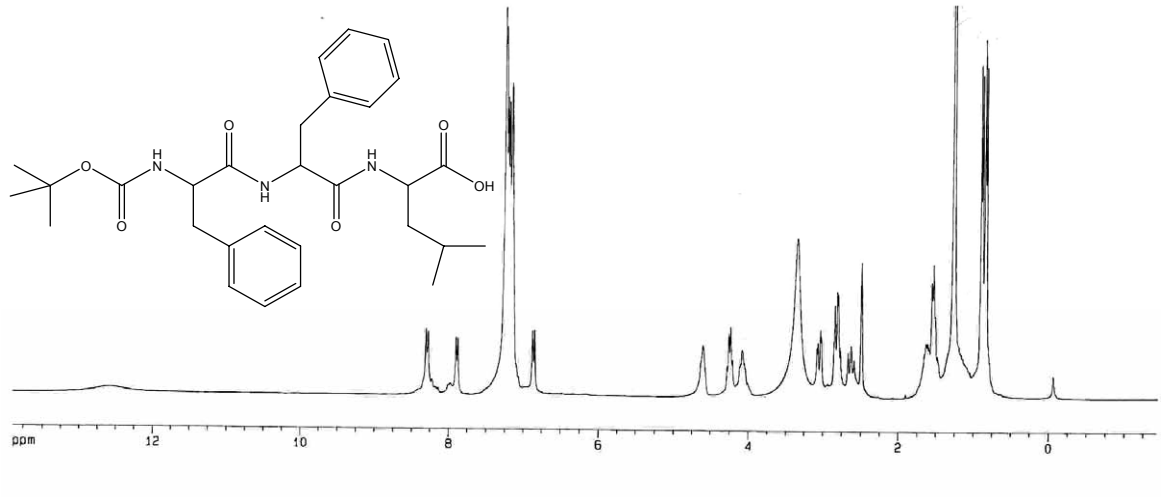


Figure S4: 300 MHz NMR Spectrum of Peptide **2**

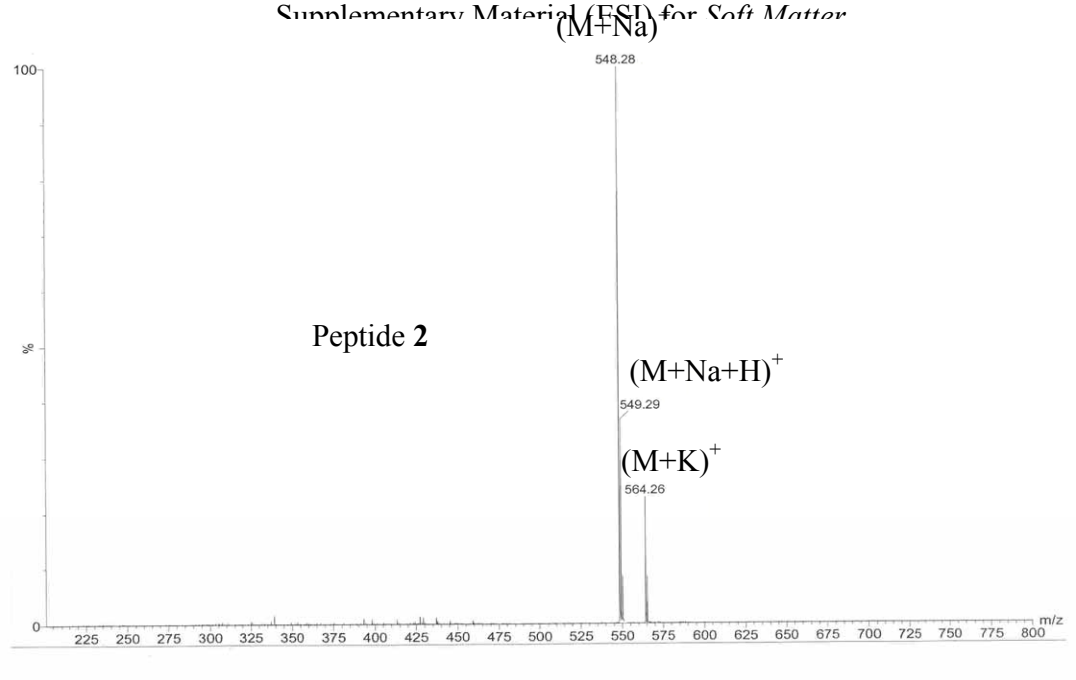


Figure S5: ESI-MS Spectrum of Peptide **2**

Figure S6: ^{13}C NMR Spectrum of Peptide **2**

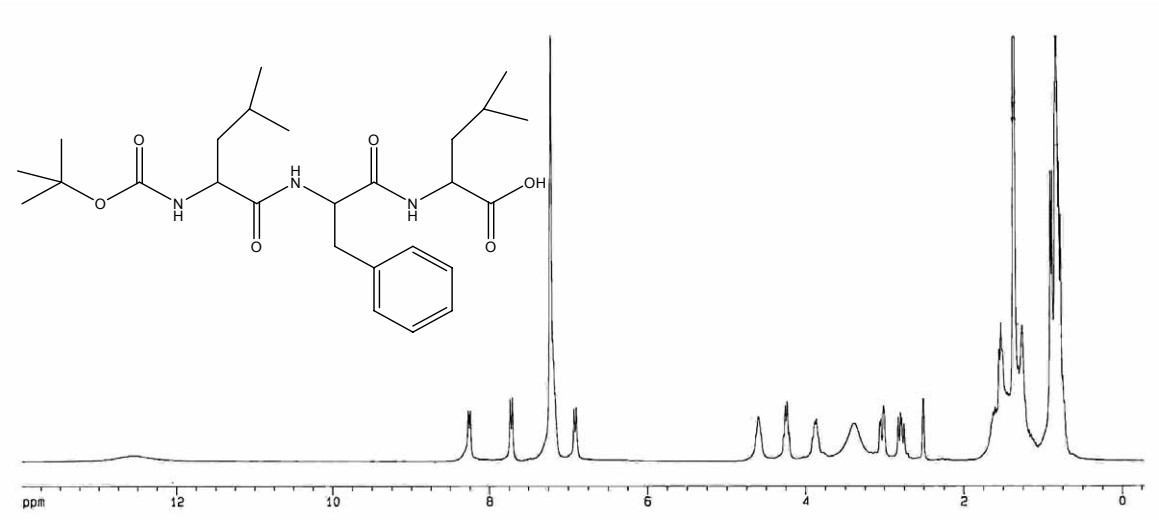


Figure S7: 300 MHz NMR Spectrum of Peptide **3**

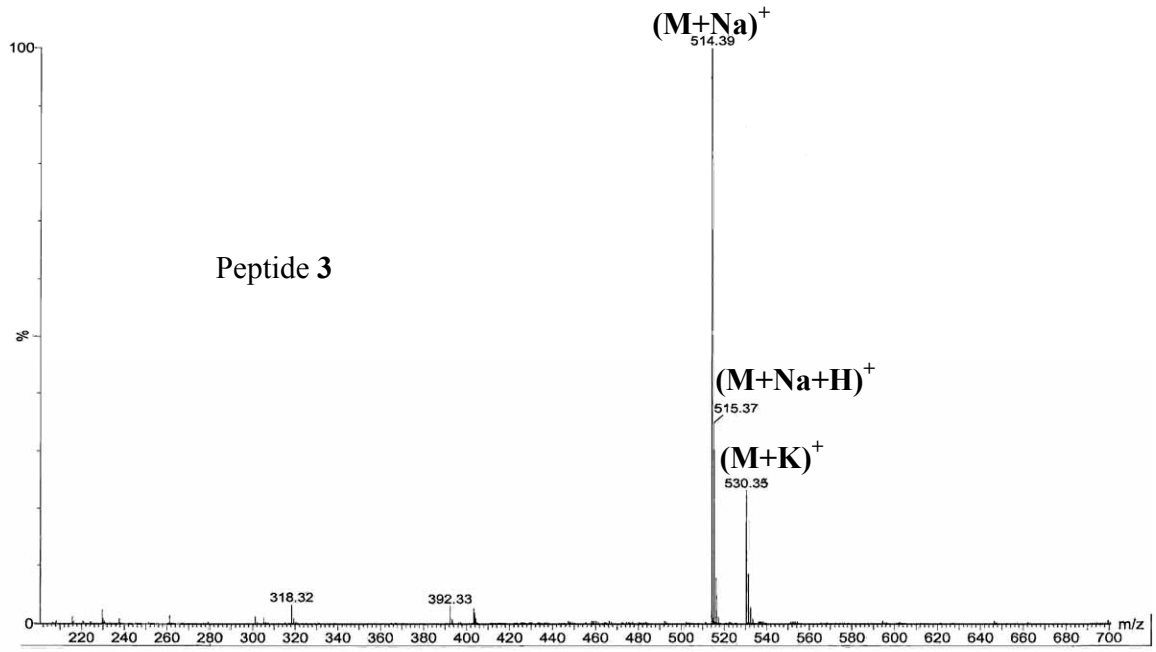


Figure S8: ESI-MS Spectrum of Peptide **3**

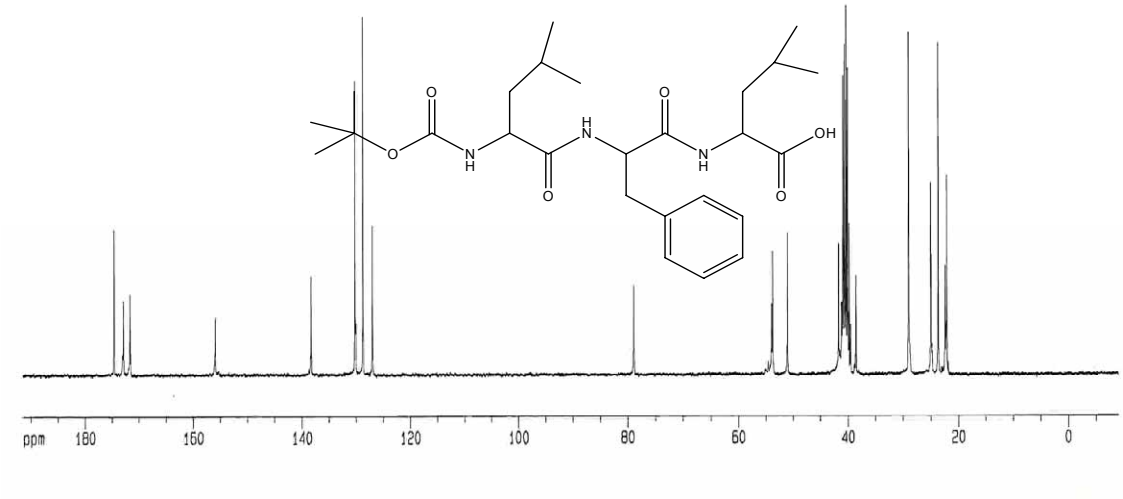


Figure S9: ^{13}C NMR Spectrum of Peptide **3**

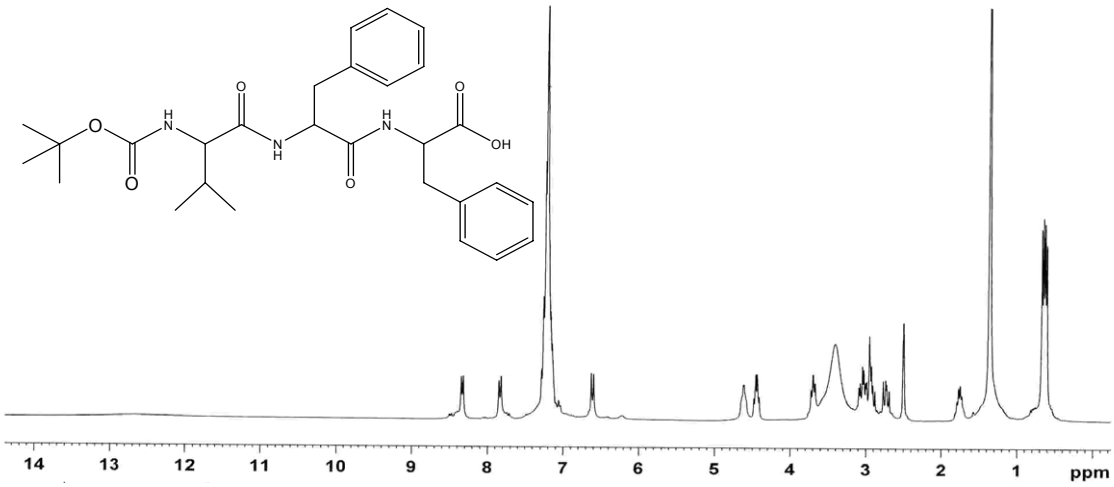


Figure S10: 300 MHz NMR Spectrum of Peptide **4**

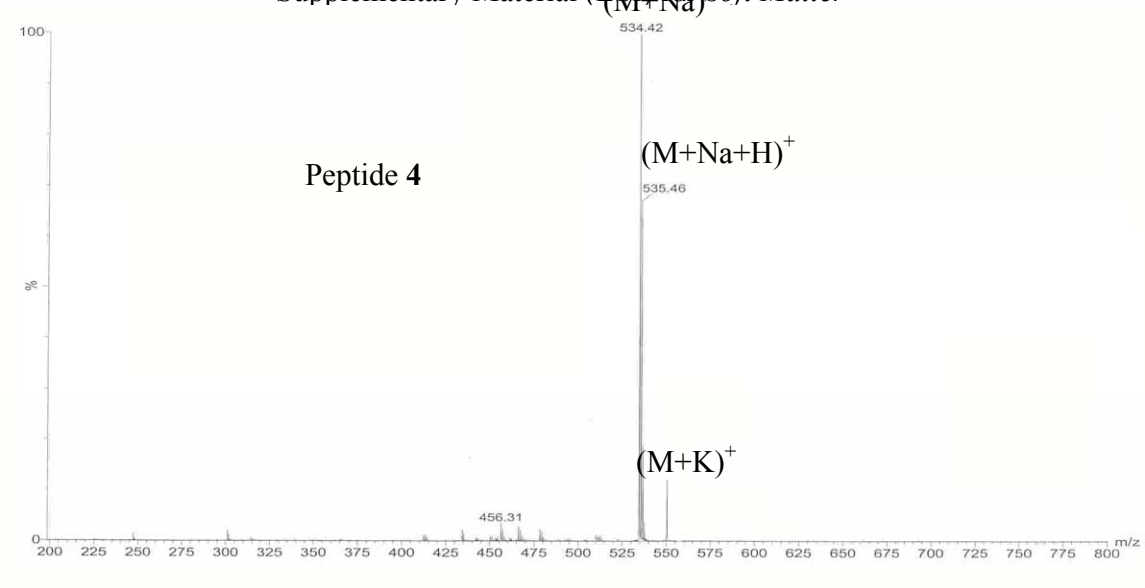


Figure S11: ESI-MS Spectrum of Peptide **4**

Figure S12: ^{13}C NMR Spectrum of Peptide **4**

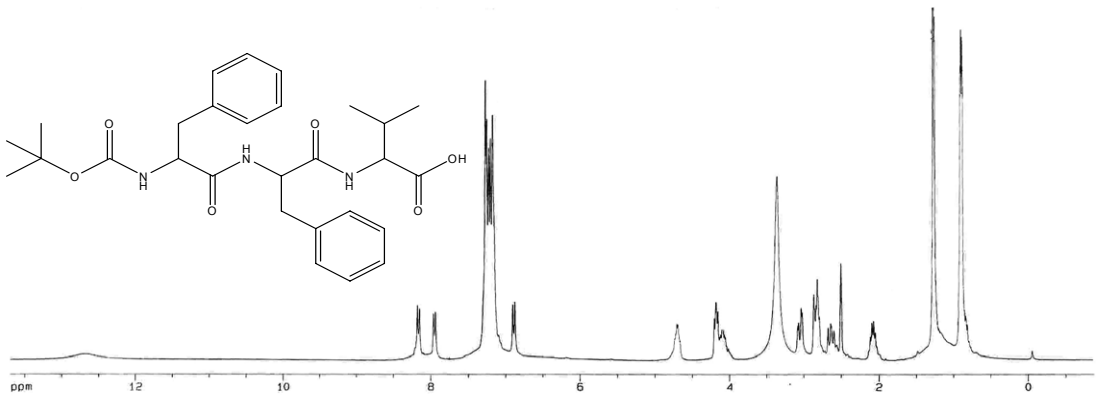


Figure S13: 300 MHz NMR Spectrum of Peptide **5**

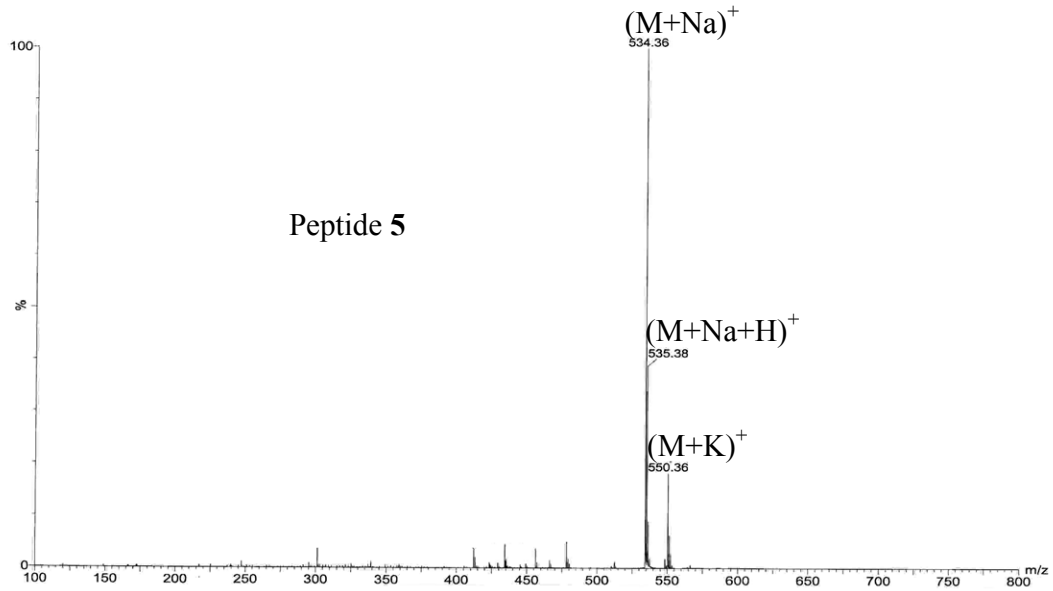


Figure S14: ESI-MS Spectrum of Peptide **5**

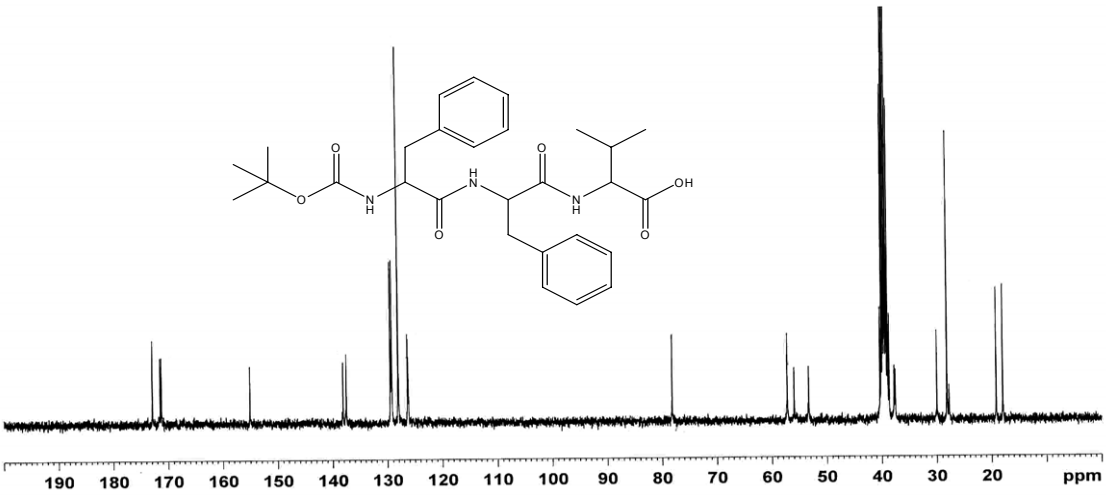


Figure S15: ^{13}C NMR Spectrum of Peptide **5**

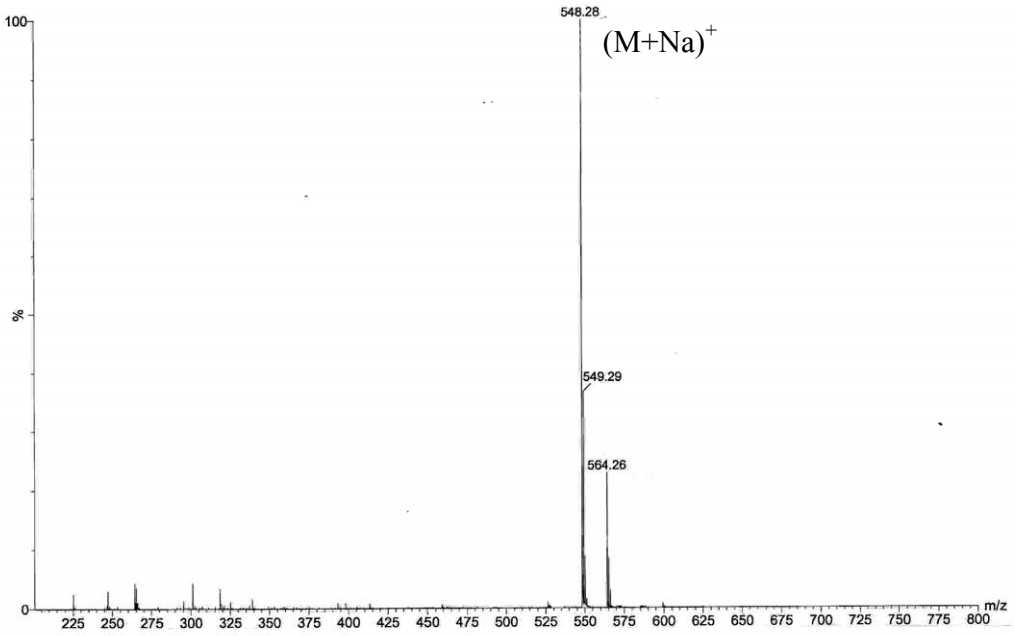


Figure S16: ESI-MS Spectrum of Peptide **2** after recovery from dye encapsulated gel material.

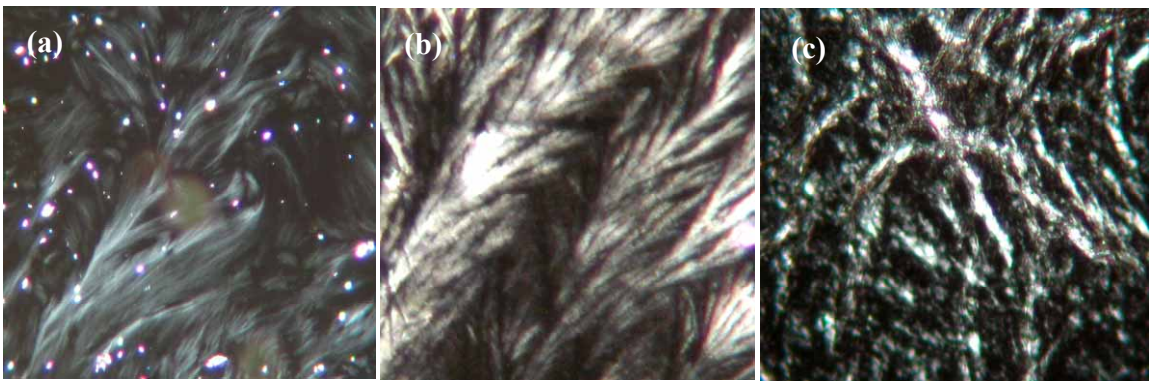


Figure S17: POM images of hydrogels obtained from: (a) Peptide **1**; (b) Peptide **2** and (c) Peptide **3**.

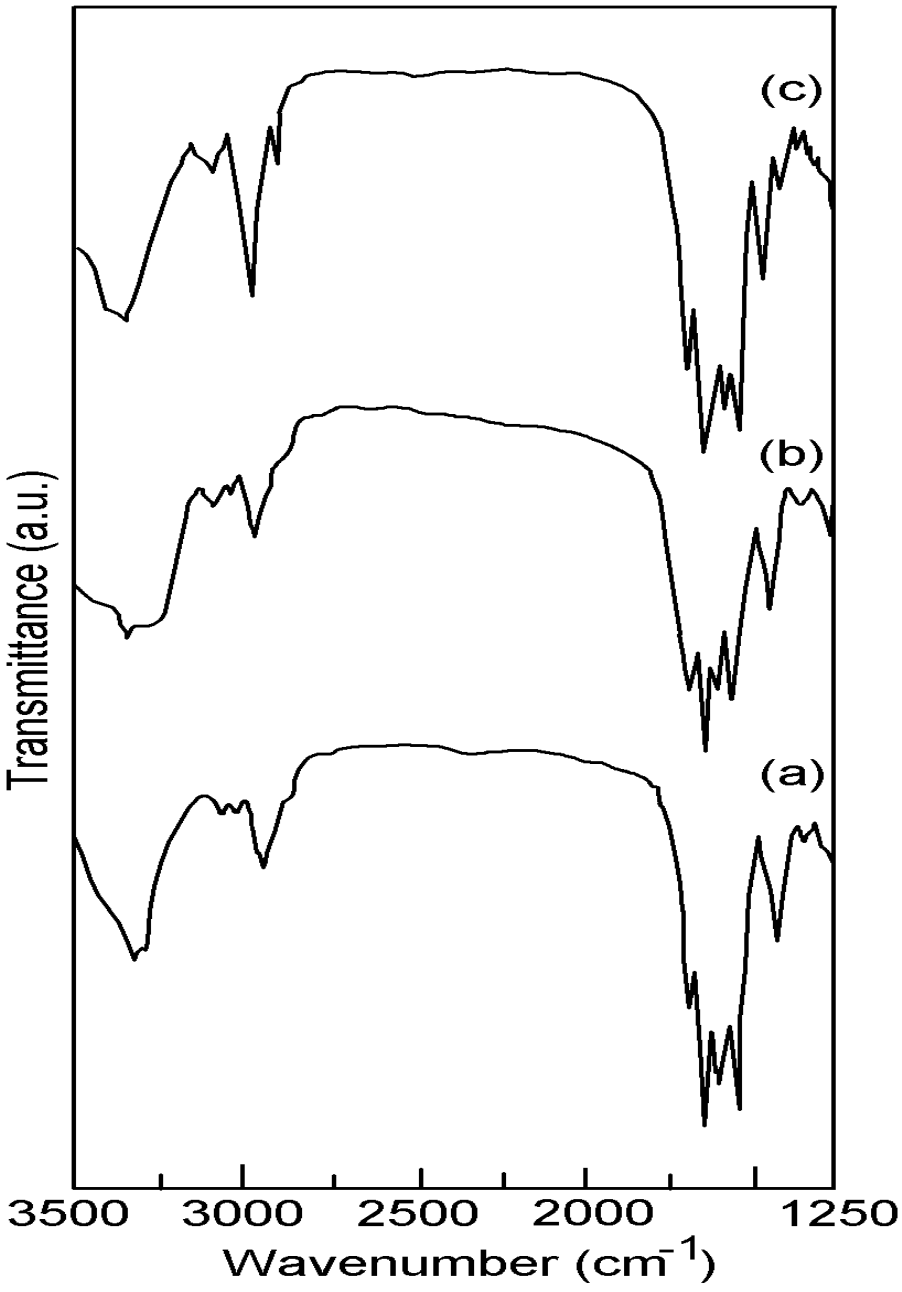


Figure S18: FT-IR spectra of Xerogels obtained from: (a) Peptide **1**; (b) Peptide **2** and (c) Peptide **3**.

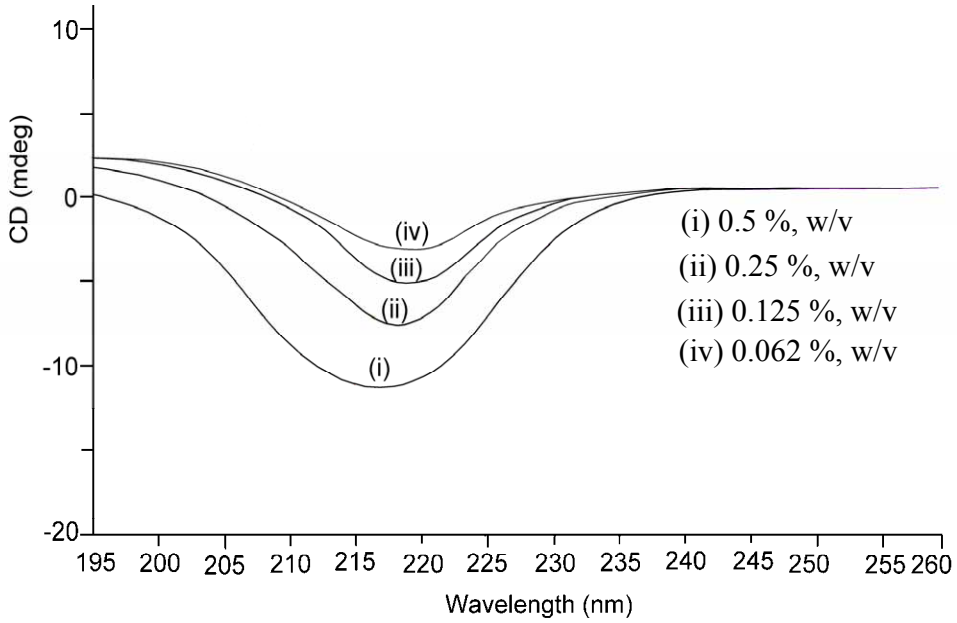
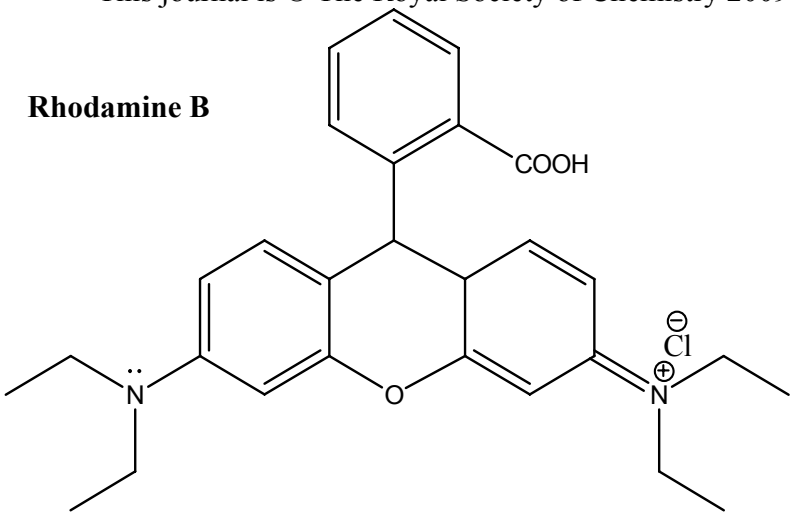
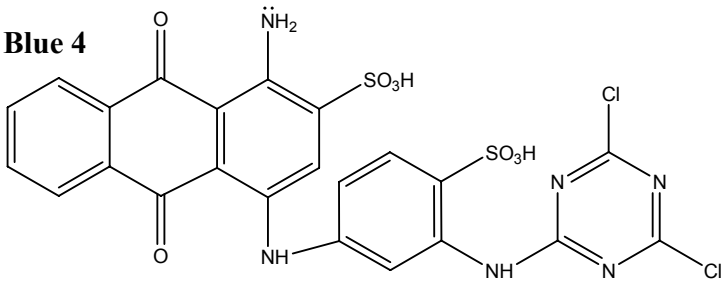


Figure S19: CD spectra obtained from Peptide **2** with varying concentrations at room temperature.

Rhodamine B



Reactive Blue 4



Direct Red 80

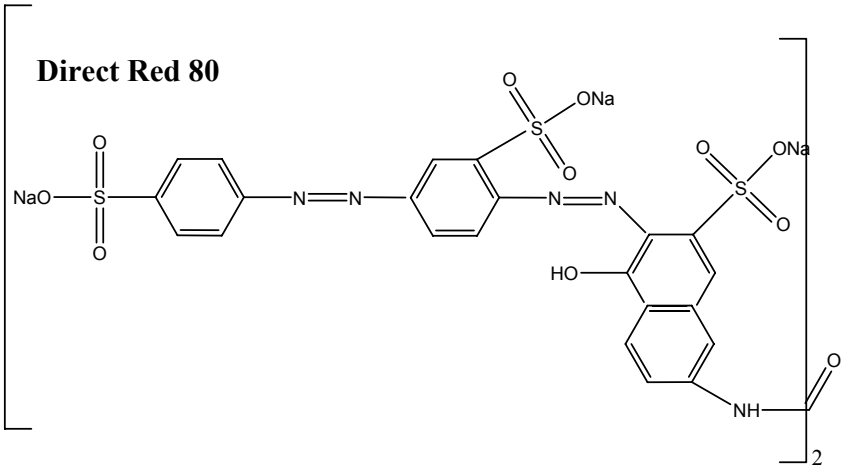


Figure S20: Chemical structures of dyes available in waste-water.

Tables:

Table S1. Major peaks found in FT-IR spectra of bulk solid, wet gel and xerogel obtained from peptides **1, 2** and **3.**

	Gelator Peptide	Amide A (NH stretching) cm^{-1}	Amide I (>C=O stretching) cm^{-1}	Amide II (NH bending) cm^{-1}	>C=O stretching of –COOH (carboxylic acid) cm^{-1}	>C=O stretching of $–COO^-$ (carboxylate anion) cm^{-1}
Bulk solid	Peptide **1**	3357	1693, 1649	1524	1719	—
	Peptide **2**	3353	1692, 1648	1527	1719	—
	Peptide **3**	3352	1693, 1649	1528	1721	—
Wet gels obtained from	Peptide **1**	3295	1686, 1638	1541	—	1397, 1570
	Peptide **2**	3298	1684, 1636	1539	—	1397, 1570
	Peptide **3**	3298	1690, 1636	1541	—	1398, 1571
Xerogels obtained from	Peptide **1**	3332	1691, 1642	1540	—	1401, 1587
	Peptide **2**	3341	1692, 1639	1543	—	1399, 1586
	Peptide **3**	3343	1692, 1640	1543	—	1395, 1587

Table S2. Major Peaks found in the XRD pattern for Peptides **1**, **2** & **3**.

Compounds	**d-spacing (Å)**
Peptide **1**	Wet gel: 38.4, 16.43, 13.97, 3.06 Dried gel: 23.55, 17.94, 15.94, 11.63, 10.34, 7.75, 5.45, 4.64, 3.86, 2.57, 2.18
Peptide **2**	Wet gel: 39.62, 19.38, 14.57, 6.67, 4.7, 3.07 Dried gel: 23.69, 12.20, 7.39, 4.62, 3.28, 3.20, 2.51, 2.18
Peptide **3**	Wet gel: 40.13, 12.26, 4.7, 3.18, 2.49, 2.14 Dried gel: 22.44, 11.58, 4.61, 3.13

References.

S1. M. Bodanszky and A. Bodanszky, *The Practice of Peptide Synthesis*, Springer-Verlag: New York, 1984, pp 1–282.

S2. A. Banerjee, G. Palui and A. Banerjee, *Soft Matter*, 2008, **4**, 1430–1437.

S3. S. Ray, M. G. B. Drew, A. K Das and A. Banerjee, *Tetrahedron*, 2006, **62**, 7274–7283.