Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information

Sonication induced peptide-appended bolaamphiphile hydrogels for *in situ* generation and catalytic activity of Pt nanoparticles

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Synthesis of Gelators

Synthesis of HO-Tyr(4)-Leu(3)-Suc-Phe(1)-Tyr(2)-OH 1

HO-Suc-Phe(1)-OMe 4

1.5 g (15 mmol) succinic anhydride in 3 ml of DMF were cooled in an ice-water bath and H-Phe-OMe was isolated from 3.23 g (15 mmol) of the corresponding methyl ester hydrochloride by neutralization and subsequent extraction by ethyl acetate and the ethyl acetate extract was concentrated to 8 ml. It was then added to the reaction mixture, followed immediately by 1.51 g (15 mmol, 1 ml 650 µl) N-methyl morpholine. The reaction mixture was stirred for overnight. 50 ml ethyl acetate was added to the reaction mixture and the organic layer was washed with 1M HCl (3 X 50 ml.). The ethyl acetate part was dried over anhydrous Na_2SO_4 and was filtered. It was evaporated in vacuo to yield **4** as sticky compound. Purification was done by silica gel column (100–200 mesh) using chloroform–methanol as eluent.

Yield: 3.56 g (12.75 mmol, 85 %); R_f 0.75 ($CHCl_3$:CH_3OH:CH_3COOH = 10:2:0.1); FT-IR (KBr): γ = 3307 (s), 3085(m), 1731 (ms), 1652 (s), 1540 (s) cm^{-1} ; ^1H NMR (300 MHz, DMSO-d_6, δ): 8.32 - 8.30 (d, J = 7.5 Hz, 1H, NH of Phe(1)), 7.15 - 7.26 (m, 5Hs, aromatic ring protons of Phe(1)), 4.43 - 4.36 (m, 1H, C^{α} H of Phe(1)), 3.62 (s, 3H, COOC$\underline{H}_3$), 2.99 - 2.97 (d, J = 5.7 Hz, 2H, C^{β} Hs of Phe(1)), 2.46 - 2.36 (m, 4H, -C$\underline{H}_2$- of Suc); $[\alpha]_D^{20}$ = +11.47 (c = 1 in CH_3OH); ESI (m/z (%)): 279.0 (20) [M^+], 278.0 (100) [M^+ - H].

MeO-Leu(2)-Suc-Phe(1)-OMe 5

3.35 g (12 mmol) of HO-Suc-Phe(1)-OMe **4** in 3 ml of DMF were cooled in an ice–water bath and H-Leu-OMe was isolated from 4.3 g (24 mmol) of the corresponding methyl ester hydrochloride by neutralization and subsequent extraction with ethyl acetate and the ethyl acetate extract was concentrated to 8 ml. It was then added to the reaction mixture, followed immediately by 2.72 g (13.2 mmol) DCC and 1.82 g (13.2 mmol) of HOBt. The reaction

mixture was stirred for overnight. The residue was taken up in ethyl acetate (50 ml) and the DCU was filtered off. The organic layer was washed with 1 M HCl (3 × 50 ml), brine (2 × 50 ml), 1 M sodium carbonate (3 × 50 ml), brine (2 × 50 ml), dried over anhydrous sodium sulfate and evaporated in vacuo to yield **5** as a white solid. Purification was done by silica gel column (100–200 mesh) using chloroform–methanol as eluent.

Yield: 4.24 g (10.44 mmol, 87 %); R_f 0.677 ($CHCl_3$:CH_3OH = 9:1); FT - IR (KBr): ν = 3328 (s), 3071 (m), 1736 (ms), 1639 (s), 1546 (s), 1528 (s) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, δ): 8.31 - 8.29 (d, J = 6.9 Hz, 1H, NH of Leu(2)), 8.17 - 8.14 (d, J = 7.5 Hz, 1H, NH of Phe(1)), 7.23 - 7.14 (m, 5H, ring protons of Phe(1)), 4.39 - 4.37 (m, 1H, $C^{\alpha}H$ of Phe(1)), 4.21 - 4.19 (m, 1H, $C^{\alpha}H$ of Leu(2)), 3.55 and 3.53 (s, 6H, -COOC$\underline{H}_3$), 2.98 - 2.96 (d, J = 5.7 Hz, 2H, $C^{\beta}Hs$ of Phe(1)), 2.45 (m, 4H,-C$\underline{H}_2$- of Suc), 1.54 -1.51 and 1.47-1.39 (m, 2H, $C^{\beta}Hs$ of Leu(2) and 1H, $C^{\gamma}H$ of Leu(2)), 0.84 - 0.76 (d, J = 6.3 Hz, 6H, $C^{\delta}Hs$ of Leu(2)); $[\alpha]_D^{20}$ = - 16.44 (c = 0.5 in CH_3OH); ESI (m/z (%)): 406.0 (10) [M^+], 405.0 (30) [M^+ - H], 373.0 (100) [M^+ - CH_3OH - H].

HO-Leu(2)-Suc-Phe(1)-OH 6

4.06 g (10 mmol) of MeO-Leu(2)-Suc-Phe(1)-OMe **5** in 6 ml MeOH was taken in a round bottom flask (R.B) and 2M NaOH was added dropwise. The reaction was monitored by thin layer chromatography (TLC). The reaction mixture was stirred for overnight. 15 ml of distilled water was added to the reaction mixture and MeOH was removed under vacuo. The aqueous part was washed with diethyl ether (2 x 30 ml). Then it was cooled down under ice water bath for 10 minute and then pH was adjusted to 1 by drop wise addition of 1 M HCl. It was extracted with ethyl acetate (3 x 50 ml) and then the ethyl acetate part was dried over anhydrous Na_2SO_4 and evaporated in vacuo to yield **6** as a white solid. Yield: 3.63 g (9.6 mmol, 96 %); R_f 0.54 ($CHCl_3$:CH_3OH:CH_3COOH = 10:2:0.1); FT - IR (KBr): ν = 3360 (s), 3031 (m), 1721 (ms), 1614 (s), 1531 (s), 1513 (s) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6, δ):

12.4 (s, 2H of –COOH), 8.15 - 8.12 (d, J =7.8 Hz,1H, NH of Leu(2)), 8.03 - 8.00 (d, J = 7.8 Hz, 1H, NH of Phe(1)), 7.25 - 7.18 (m, 5H, ring protons of Phe(1)), 4.39 - 4.31 (m, 1H, $C^{\alpha}H$ of Phe(1)), 4.18 - 4.10 (m, 1H, $C^{\alpha}H$ of Leu(2)), 3.02 - 3.00 (d, J = 5.1 Hz, 2H, $C^{\beta}Hs$ of Phe(1)), 2.83 - 2.75 and 2.46 - 2.36 (m, 4H, -CH_2- of Suc), 1.79 and 1.59-1.50 (m, 2H, $C^{\beta}Hs$ of Leu(2), 1H, $C^{\gamma}H$ of Leu(2)), 0.84 - 0.77 (d, J = 6.3 Hz, 6H, $C^{\delta}Hs$ of Leu(2)); $[\alpha]_D^{20}$ = +6 (c = 0.5 in CH_3OH); ESI (m/z (%)): 378.1 (25) [M^+], 377.0 (100) [M^+ - H], 755.0 (50) [2 M^+ - H].

MeO-Tyr(4)-Leu(3)-Suc-Phe(1)-Tyr(2)-OMe 7

1.70 g (4.5 mmol) of HO-Leu-Suc-Phe-OH **6** in 3 ml of DMF were cooled in an ice–water bath and H-Tyr-OMe was isolated from 4.17 g (18 mmol) of the corresponding methyl ester hydrochloride by neutralization and subsequent extraction with ethyl acetate and the ethyl acetate extract was concentrated to 8 ml. It was then added to the reaction mixture, followed immediately by 2.04 g (9.9 mmol) DCC and 1.33 g (9.9 mmol) of HOBt. The reaction mixture was stirred for overnight. The residue was taken up in ethyl acetate (50 ml) and the DCU was filtered off. The organic layer was washed with 1 M HCl (3 × 50 ml), brine (2 × 50 ml), 1 M sodium carbonate (3 × 50 ml), brine (2 × 50 ml), dried over anhydrous sodium sulfate and evaporated in vacuo to yield **7** as a white solid. Purification was done by silica gel column (100–200 mesh) using chloroform–methanol as eluent.

Yield: 2.70 g (3.69 mmol, 82 %); R_f 0.63 ($CHCl3:CH_3OH$ = 9:1); FT - IR (KBr): ν = 3298 (s), 3066 (ms), 1738 (ms), 1644 (s), 1540 (s), 1516 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, δ): 7.19 (m, 5H, ring protons of Phe(1)), 7.10 - 7.08 (d, J = 6 Hz, 1H, NH of Leu(3)), 6.95 - 6.89 (d, J = 8.1, J = 10.5 Hz, 4H, ring protons of Tyr(2), Tyr(4)), 6.86 - 6.84 (d, J = 7.2 Hz, 1H, NH of Phe(1)), 6.79 - 6.75 and 6.68 (d, J = 9.4, J = 7.8 Hz, 4H of Tyr(2), Tyr(4)), 6.60 - 6.57 (d, J = 8.3 Hz, 1H, NH of Tyr(4)), 6.55 - 6.52 (d, J = 8.3 Hz, 1H, NH of Tyr(2)), 4.83 (m, 1H, $C^{\alpha}H$ of Phe(1)), 4.55 and 4.53 (m, 2H, $C^{\alpha}Hs$ of Tyr(1), Tyr(4)), 4.36 - 4.34 (m, 1H, $C^{\alpha}H$ of Leu(3),

3.63 and 3.62 (s, 6H, -COOC<u>H</u>$_3$), 2.96 (d, J = 7.5 Hz, 2H, C$^{\beta}$Hs of Phe(2)), 2.94 (d, *J* = 6.9, *J* = 7.2 Hz, 4H, C$^{\beta}$Hs of Tyr(2), Tyr(4)), 2.69 - 2.66 (m, 4H, -C<u>H</u>$_2$- of Suc), 1.57 - 1.55 and 1.49 - 1.47 (m, 2H, C$^{\beta}$Hs of Leu(3), 1H, C$^{\gamma}$H of Leu(3)), 0.83 - 0.81 (d, *J* = 6.8 Hz, 6H, C$^{\delta}$Hs of Leu(3)); $[\alpha]_D^{20}$ = -30.8 (*c* = 0.5 in CH_3OH); ESI (*m/z* (%)): 732.3 (60) [M^+], 731.3 (100) [M^+ - H], 1463.8 (30) [2 M^+ - H].

HO-Tyr(4)-Leu(3)-Suc-Phe(1)-Tyr(2)-OH 1

2.56 g (3.5 mmol) of MeO-Tyr(4)-Leu(3)-Suc-Phe(1)-Tyr(2)-OMe **7** in 10 ml MeOH was taken in a round bottom flask (R.B.) and 2M NaOH was added to it dropwise. The reaction was monitored by thin layer chromatography (TLC). The reaction mixture was stirred for overnight. 15 ml of distilled water was added to the reaction mixture and MeOH was removed under vacuo. The aqueous part was washed with diethyl ether (2 x 30 ml). Then it was cooled under in ice water bath for 10 minute and then pH was adjusted to 1 by drop wise addition of 1M HCl. It was extracted by ethyl acetate (3 x 50 ml) and then the ethyl acetate part was dried over anhydrous Na_2SO_4 and evaporated in vacuo to yield **1** as a white solid. Yield: 2.21 g (3.15 mmol, 90%); R_f 0.26 ($CHCl_3$:CH_3OH:CH_3COOH = 10:2:0.1); FT - IR (KBr): ν = 3299 (s), 1715 (m), 1645 (s), 1540 (s), 1516 (ms) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, δ): 12.59 (s, 2H of –COO<u>H</u>), 8.18 - 8.16 (d, *J* = 7.5 Hz,1H, NH of Leu(3)), 8.03 - 8.01 (d, *J* = 8.4 Hz, 1H, NH of Phe(1)), 7.98 - 7.96 (d, *J* = 7.5 Hz, 1H, NH of Tyr(4)), 7.91 - 7.88 (d, *J* = 8.4 Hz, 1H, NH of Tyr(2)), 7.22 - 7.16 (m, 5H, ring protons of Phe(1)), 7.02 (d, *J* = 8.4 Hz, 2H, ring protons of Tyr(4)), 7.00 (d, *J* = 8.4 Hz, 2H, ring protons of Tyr(4)), 6.67 (d, *J* = 8.1 Hz, 2H, ring protons of Tyr(2)), 6.64 (d, *J* = 6.6 Hz, 2H, ring protons of Tyr(2)), 4.50 (m, 1H, C$^{\alpha}$H of Phe(1)), 4.35 - 4.30 (m, 2H, C$^{\alpha}$Hs of Tyr(2), Tyr(4)), 4.04 - 4.02 (m, 1H, C$^{\alpha}$H of Leu(3)), 2.97 (d, *J* = 8.4 Hz, 2H, C$^{\beta}$Hs of Phe(1)), 2.92 - 2.80 (d, *J* = 5.4, *J* = 5.7 Hz, 4H, C$^{\beta}$Hs of Tyr(2), Tyr(4)), 2.71 - 2.68 (m, 4H, -C<u>H</u>$_2$- of Suc), 1.91 and 1.37 - 1.35 (m, 2H, C$^{\beta}$Hs of Leu(3), 1H, C$^{\gamma}$H of Leu(3)), 0.81 - 0.79 (d, *J* = 6.3 Hz, 6H, C$^{\delta}$Hs of Leu(3)), ^{13}C NMR (75

MHz, DMSO-d_6, δ_{ppm}): 173.07 (C=O), 171.43 (C=O), 162.05 (C=O), 156.14 (C=O), 138.15, 130.26, 129.39, 128.17, 117.89, 115.15, 53.93, 50.93, 40.54, 40.26, 39.98, 39.70, 39.43, 39.15, 38.87, 31.01, 23.25, 21.82; $[\alpha]_D^{20}$ = -15.35 (*c* = 0.5 in CH_3OH); ESI (*m/z* (%)): 703.2 (100) [M^+ - H].

MeO-Phe(4)-Leu(3)-Suc-Phe(1)-Phe(2)-OMe 8

1.70 g (4.5 mmol) of HO-Leu(2)-Suc-Phe(1)-OH **6** in 3 ml of DMF were cooled in an ice–water bath and H-Phe-OMe was isolated from 3.88 g (18 mmol) of the corresponding methyl ester hydrochloride by neutralization and subsequent extraction with ethyl acetate and the ethyl acetate extract was concentrated to 8 ml. It was then added to the reaction mixture, followed immediately by 2.04 g (9.9 mmol) DCC and 1.33 g (9.9 mmol) of HOBt. The reaction mixture was stirred for overnight. The residue was taken up in ethyl acetate (50 ml) and the DCU was filtered off. The organic layer was washed with 1 M HCl (3 × 50 ml), brine (2 × 50 ml), 1 M sodium carbonate (3 × 50 ml), brine (2 × 50 ml), dried over anhydrous sodium sulfate and evaporated in vacuo to yield **8** as a white solid. Purification was done by silica gel column (100–200 mesh) using chloroform–methanol as eluent and white solid product was obtained.

Yield: 2.45 g (3.51 mmol, 78 %); R_f 0.81 ($CHCl_3$:CH_3OH = 9:1); FT - IR (KBr): ν = 3321 (s), 1743 (ms), 1634 (s), 1539 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.19 - 7.02 (m, 15H, ring protons of Phe(1), Phe(2) and Phe(4)), 6.96 - 6.93 (d, *J* = 8.4 Hz, 1H, NH of Leu(3)), 6.78 - 6.75 (d, *J* = 8.1 Hz, 1H, NH of Phe(4)), 6.40 - 6.37 (d, *J* = 8.1 Hz, 1H, NH of Phe(1)), 6.28 - 6.25 (d, *J* = 8.1 Hz , 1H, NH of Phe(2)), 4.80 - 4.72 (m, 2H, C^{α}Hs of Phe(2) and Phe(1)), 4.62 - 4.60 (m,1H, C^{α}H of Phe(4)), 4.40 - 4.39 (m, 1H, C^{α}H of Leu(3), 3.65 - 3.62 (s, 6H of $COOC\underline{H}_3$), 3.07 - 2.99 and 2.96 - 2.89 (d, *J* = 6, *J* = 5.7, *J* = 6.3 Hz, 6H, C^{β}Hs of Phe(1), Phe(2) and Phe(4)), 2.44 - 2.31 (m, 4H, -$C\underline{H}_2$- of Suc), 1.56 - 1.52 and 1.35 - 1.32 (m, 2H, C^{β}Hs of Leu(3), 1H, C^{γ}H of Leu(3)), 0.81 - 0.79 (d, *J* = 5.4 Hz, 6H, C^{δ}Hs of Leu(3)); ^{13}C

NMR (75 MHz, $CDCl_3$, δ_{ppm}): 172.05 (C=O), 171.78 (C=O), 170.77 (C=O), 162.30 (C=O), 136.57, 135.91, 129.31, 129.20, 128.55, 128.49, 127.01, 126.87, 77.41, 77.18, 76.98, 76.56, 54.49, 53.39, 53.22, 52.25, 51.94, 40.83, 37.89, 31.53, 24.71, 22.78, 21.97; $[\alpha]_D^{20}$ = + 8.23 (*c* = 0.5 in $CHCl_3$); ESI (*m/z* (%)): 700.2 (25) [M^+], 699.3 (100) [M^+ - H].

Synthesis of HO-Phe(4)-Leu(3)-Suc-Phe(1)-Phe(2)-OH 2

2.24 g (3.2 mmol) of MeO-Phe(4)-Leu(3)-Suc-Phe(1)-Phe(2)-OMe **8** in 150 ml MeOH was taken in a round bottom flask (R.B) and 2M NaOH was added dropwise. The reaction was monitored by thin layer chromatography (TLC). The reaction mixture was stirred for overnight. 15 ml distilled water was added to the reaction mixture and MeOH was removed under vacuo. The aqueous part was washed with diethyl ether (2 x 30 ml). Then it was cooled under ice-water bath for 10 minute and then pH was adjusted to 1 by drop wise addition of 1 M HCl. It was extracted with ethyl acetate (3 x 50 ml) and then the ethyl acetate part was dried over anhydrous Na_2SO_4 and evaporated in vacuo to yield **2** as a white solid. Yield: 1.97 g (2.94 mmol, 92 %); R_f 0.35 ($CHCl_3$:CH_3OH:CH_3COOH = 10:2:0.1); FT - IR (KBr): ν = 3296 (s), 1716 (ms), 1638 (s), 1538 (s) cm^{-1} ; ^1H NMR (300 MHz, DMSO-d_6, δ): 8.20 - 8.18 (d, *J* = 7.5 Hz, 1H, NH of Leu(3)), 8.01 and 7.96 (d, *J* = 6.9 Hz, *J* = 8.1 Hz , 2H, NH of Phe(2), Phe(1)), 7.85 - 7.82 (d, *J* = 7.8 Hz, 1H, NH of Phe(4)), 7.21 - 7.16 (m, 15 H, ring protons of Phe(1), Phe(2) and Phe(4)), 4.46 - 4.32 (m, 3H, $C^{\alpha}Hs$ of Phe(1), (Phe(2) and Phe(4)), 4.23 - 4.21 (m, 1H, $C^{\alpha}H$ of Leu(3), 3.04, 2.99 and 2.96 (d, *J* = 5.1, *J* = 4.8, *J* = 5.7 Hz, 6H, $C^{\beta}Hs$ of Phe(1), Phe(2) and Phe(4)), 2.44 - 2.43 (m, 4H, -$C\underline{H}_2$- of Suc), 1.47 and 1.33 - 1.31 (m, 2H, $C^{\beta}Hs$ of Leu(3), 1H, $C^{\gamma}H$ of Leu(3)), 0.79 - 0.77 (d, *J* = 6.3 Hz, 6H, $C^{\delta}Hs$ of Leu(3)), ^{13}C NMR (75 MHz, DMSO-d_6 δ_{ppm}): 172.84 (C=O), 172.18 (C=O), 171.40 (C=O), 171.30 (C=O), 142.46, 138.06, 137.61, 129.26, 128.31, 128.24, 128.06, 126.49, 126.27, 117.78, 53.63, 53.45, 50.82, 40.82, 40.43, 40.16, 39.88, 39.60, 39.32, 39.05, 38.77, 36.62,

30.79, 24.20, 23.11, 21.74; $[\alpha]_D^{20}$ = - 17.3 (*c* = 0.5 in CH_3OH); ESI (*m/z* (%)): 672.2 (30) [M^+], 671.2 (100) [M^+ - H].

HO- Suc-Leu(1)-OMe 9

1.007 g (10 mmol) succinic anhydride in 3 ml of DMF were cooled in an ice-water bath and H-Leu-OMe was isolated from 1.81 g (10 mmol) of the corresponding methyl ester hydrochloride by neutralization and subsequent extraction by ethyl acetate and the ethyl acetate extract was concentrated to 8 ml. It was then added to the reaction mixture, followed immediately by 1.011 g (10 mmol, 1 ml 100 µl) N-methyl morpholine. The reaction mixture was stirred for overnight. 50 ml ethyl acetate was added to the reaction mixture and the organic layer was washed with 1M HCl (3 X 50 ml.). The ethyl acetate part was dried over anhydrous Na_2SO_4 and was filtered. It was evaporated in vacuo to yield **4** as sticky compound. Purification was done by silica gel column (100–200 mesh) using chloroform–methanol as eluent.

Yield: 1.96 g (8 mmol, 80 %); R_f 0.58 ($CHCl_3$:CH_3OH:CH_3COOH = 10:2:0.1); FT - IR (KBr): γ = 3232 (s), 3059 (m), 1731 (ms), 1648 (s), 1558 (s), 1524 (s) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, δ): 8.19 - 8.16 (d, *J* = 7.5 Hz, 1H of NH of Leu(1)), 4.26 - 4.21 (m, 1H, $C^{\alpha}H$ of Leu(1)), 3.52 (s, 3H, $COOC\underline{H}_3$), 2.46 - 2.36 (m, 4H, -$C\underline{H}_2$- of Suc), 1.59 - 1.50 and 1.48 - 1.40 (m, 2H, $C^{\beta}Hs$ of Leu(1), 1H, $C^{\gamma}H$ of Leu(1)), 0.85 - 0.82 (d, *J* = 6.6 Hz, 6H, $C^{\delta}Hs$ of Leu(1)); $[\alpha]_D^{20}$ = - 6.08 (*c* = 1 in CH_3OH); ESI (*m/z* (%)): 245.1 (20) [M^+], 244.0 (100) [M^+ - H].

MeO-Val(2)-Suc-Leu(1)-OMe 10

1.71 g (7 mmol) of HO-Suc-Leu(1)-OMe **9** in 3 ml of DMF were cooled in an ice–water bath and H-Val-OMe was isolated from 2.33 g (14 mmol) of the corresponding methyl ester hydrochloride by neutralization and subsequent extraction with ethyl acetate and the ethyl

acetate extract was concentrated to 8 ml. It was then added to the reaction mixture, followed immediately by 1.58 g (7.7 mmol) DCC and 1.04 g (7.7 mmol) of HOBt. The reaction mixture was stirred for overnight. The residue was taken up in ethyl acetate (50 ml) and the DCU was filtered off. The organic layer was washed with 1 M HCl (3 × 50 ml), brine (2 × 50 ml), 1 M sodium carbonate (3 × 50 ml), brine (2 × 50 ml), dried over anhydrous sodium sulfate and evaporated in vacuo to yield **10** as a white solid. Purification was done by silica gel column (100–200 mesh) using chloroform–methanol as eluent.

Yield: 1.88 g (5.25 mmol, 75 %); R_f 0.75 ($CHCl_3$: CH_3OH = 9:1); FT - IR (KBr): ν = 3266 (s), 1757 (ms), 1678 (w), 1663 (ms), 1637 (ms), 1560 (s), 1538 (s) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, δ): 8.18 - 8.16 (d, J = 7.5 Hz, 1H, NH of Val(2)), 8.10 - 8.07 (d, J = 8.1 Hz, 1H, NH of Leu(1)), 4.25 - 4.19 (m, 1H, $C^{\alpha}H$ of Leu(1)), 4.18 - 4.08 (m, 1H, $C^{\alpha}H$ of Val(2)), 3.58 and 3.56 (s, 6H, COOC$\underline{H}_3$), 2.46 - 2.40 (m, 4H, -C$\underline{H}_2$- of Suc), 2.35 - 2.25 (m, 1H, $C^{\beta}H$ of Val(2)), 1.58 - 1.52 and 1.49 - 1.40 (m, 2H, $C^{\beta}Hs$ of Leu(1), 1H, $C^{\gamma}H$ of Leu(1)), 0.79 - 0.77 (d, J = 6.3 Hz, 6H, $C^{\delta}Hs$ of Leu(1) and 6H of $C^{\gamma}Hs$ of Val(2)); $[\alpha]_D^{20}$ = - 37.9 (c = 0.5 in CH_3OH); HRMS (ESI, *m/z*): $(M + Na)^+$ Calcd for $C_{17}H_{30}N_2O_6Na$, 381.1996; found 381.2009.

HO-Val(2)-Suc-Leu(1)-OH 11

1.72 g (4.8 mmol) of MeO-Val(2)-Suc-Leu(1)-OMe **10** in 6 ml MeOH was taken in a round bottom flask (R.B) and 2M NaOH was added to it dropwise. The reaction was monitored by thin layer chromatography(TLC). The reaction mixture was stirred for overnight. 15 ml of distilled water was added to the reaction mixture and MeOH was removed under vacuo. The aqueous part was washed with diethyl ether (2 x 30 ml). Then it was cooled under ice-water bath for 10 minute and then pH was adjusted to 1 by drop wise addition of 1M HCl. It was

extracted with ethyl acetate (3 x 50 ml) and then the ethyl acetate part was dried over anhydrous Na_2SO_4 and evaporated in vacuo to yield **11** as a white solid. Yield: 1.50 g (4.56 mmol, 95 %); R_f 0.67 ($CHCl_3$:CH_3OH:CH_3COOH = 10:2:0.1); FT - IR (KBr): ν = 3338 (s), 3065 (m), 1715 (ms), 1617 (s), 1534 (s) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, δ): 8.05 - 8.02 (d, J = 7.8 Hz, 1H, NH of Val(2)), 7.95 - 7.92 (d, J = 8.4 Hz, 1H, NH of Leu(1)), 4.16 - 4.14 (m, 1H, $C^{\alpha}H$ of Leu(1)), 4.11 - 4.06 (m, 1H, $C^{\alpha}H$ of Val(2)), 2.46 - 2.32 (m, 4H, -C$\underline{H_2}$ of Suc); 2.31 - 2.25 (m, 1H, $C^{\beta}H$ of Val(2)); 1.57 and 1.45 - 1.43 (m, 2H, $C^{\beta}Hs$ of Leu(1) and 1H, $C^{\gamma}H$ of Leu(1)), 0.85 - 0.83 (d, J = 5.7 Hz, 6H of $C^{\gamma}Hs$ of Val(2)), 0.83 - 0.81 (d, J = 6.6 Hz, 6H, $C^{\delta}Hs$ of Leu(1)); $[\alpha]_D^{20}$ = - 11.8 (c = 0.5 in CH_3OH); ESI (m/z (%)): 330.1 (20) [M^+], 329.1 (100) [M^+ - H], 659.1 (20) [$2M^+$ – H].

MeO-Phe(4)-Val(3)-Suc-Leu(1)-Phe(2)-OMe 12

1.32 g (4 mmol) of HO-Val(2)-Suc-Leu(1)-OH **11** in 3 ml of DMF were cooled in an ice-water bath and H-Phe-OMe was isolated from 3.45 g (16 mmol) of the corresponding methyl ester hydrochloride by neutralization and subsequent extraction with ethyl acetate and the ethyl acetate extract was concentrated to 8 ml. It was then added to the reaction mixture, followed immediately by 1.81 g (8.8 mmol) DCC and 1.18 g (8.8 mmol) of HOBt. The reaction mixture was stirred for overnight. The residue was taken up in ethyl acetate (50 ml) and the DCU was filtered off. The organic layer was washed with 1 M HCl (3 × 50 ml), brine (2 × 50 ml), 1 M sodium carbonate (3 × 50 ml), brine (2 × 50 ml), dried over anhydrous sodium sulfate and evaporated in vacuo to yield **12** as a white solid. Purification was done by silica gel column (100–200 mesh) using chloroform–methanol as eluent to get white solid as product.

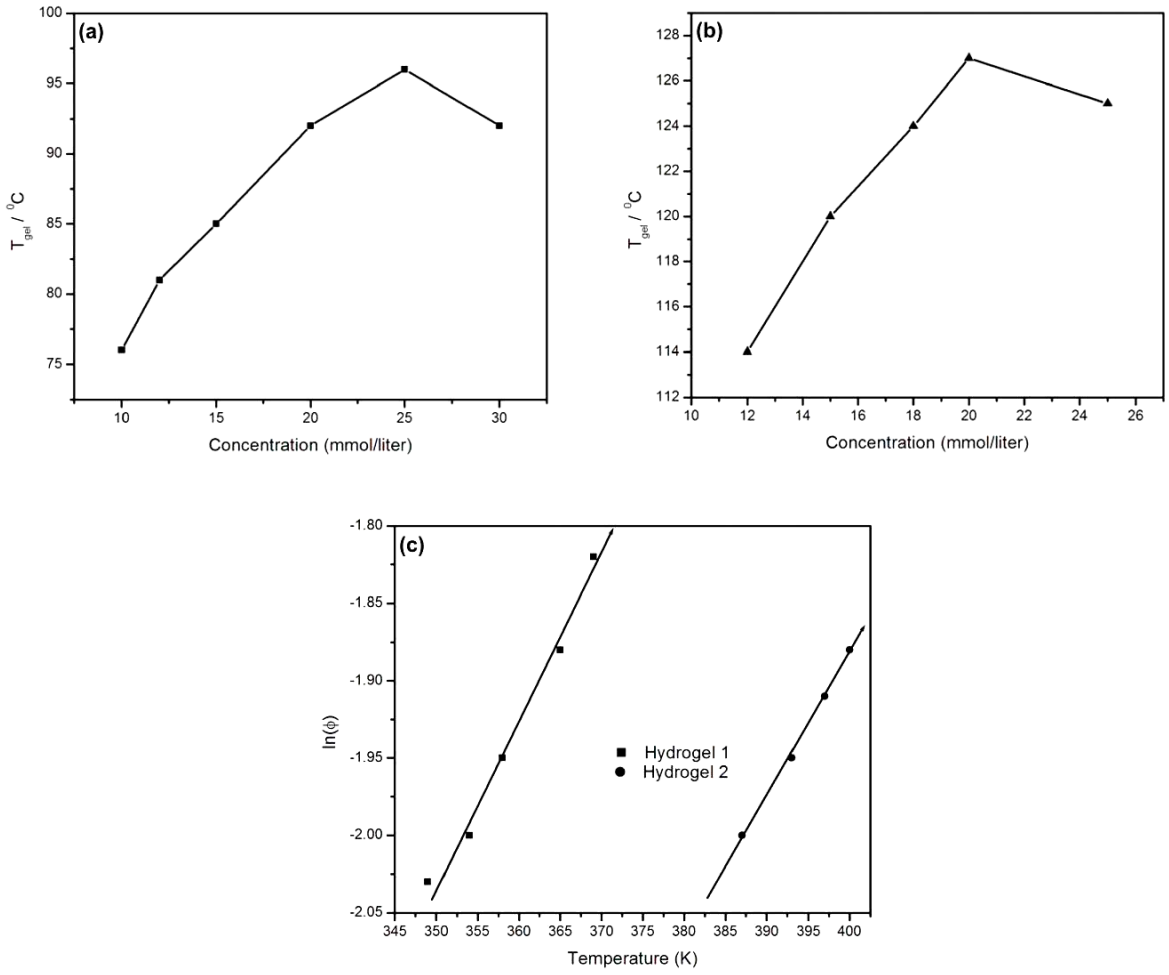
Yield: 1.98 g (3.04 mmol, 76 %); R_f 0.72 ($CHCl_3$: CH_3OH = 9:1); FT - IR (KBr): ν = 3291(s), 1747 (ms), 1631 (s), 1541 (s) cm^{-1} ; ^1H NMR (300 MHz, $CDCl_3$, δ): 7.8 (d, J = 7.5 Hz, 1H, -NH of Val (3)), 7.6 (d, J = 7.5 Hz, 1H, -NH of Leu(1)), 7.23 - 7.06 (m, 10 H, ring protons of

Phe (2) and Phe (4)), 6.6 (d, *J* = 7.8 Hz, 1H, -NH of Phe (4)), 6.32 (d, *J* = 7.5 Hz, -NH of Phe (2)), 4.82-4.80 (m, 2H, C^{α}Hs of Phe (2) and Phe (4)), 4.77 (m, 1H , C^{α}H of Leu (1)), 4.27 (m, 1H, C^{α}H of Val (3)), 3.62 (s, 6H, -COOC$\underline{H}_3$), 3.07 - 2.99 (d, *J* = 6.6 Hz, *J* = 6.9 Hz, 4H , C^{β}Hs of Phe (1) and Phe (4)), 2.48 -2.40 (m, 4H, -C$\underline{H}_2$- of Suc), 2.10 - 2.01 (m, 1H, C^{β}H of Val (3)), 1.56 - 1.53 and 1.35 -1.32(m, 2H, C^{β}Hs of Leu(3), 1H, C^{γ}H of Leu(3)); 0.81 (d, *J* = 5.4 Hz, 6H, C^{δ}Hs of Leu (1)), 0.70 (d, *J* = 6.6 Hz, 6H , C^{γ}Hs of Val(3)); $[\alpha]_D^{20}$ = + 6.17 (*c* = 0.3 in $CHCl_3$); ESI (*m/z* (%)): 652.3 (60) [M^+], 651.4 (100) [M^+ - H].

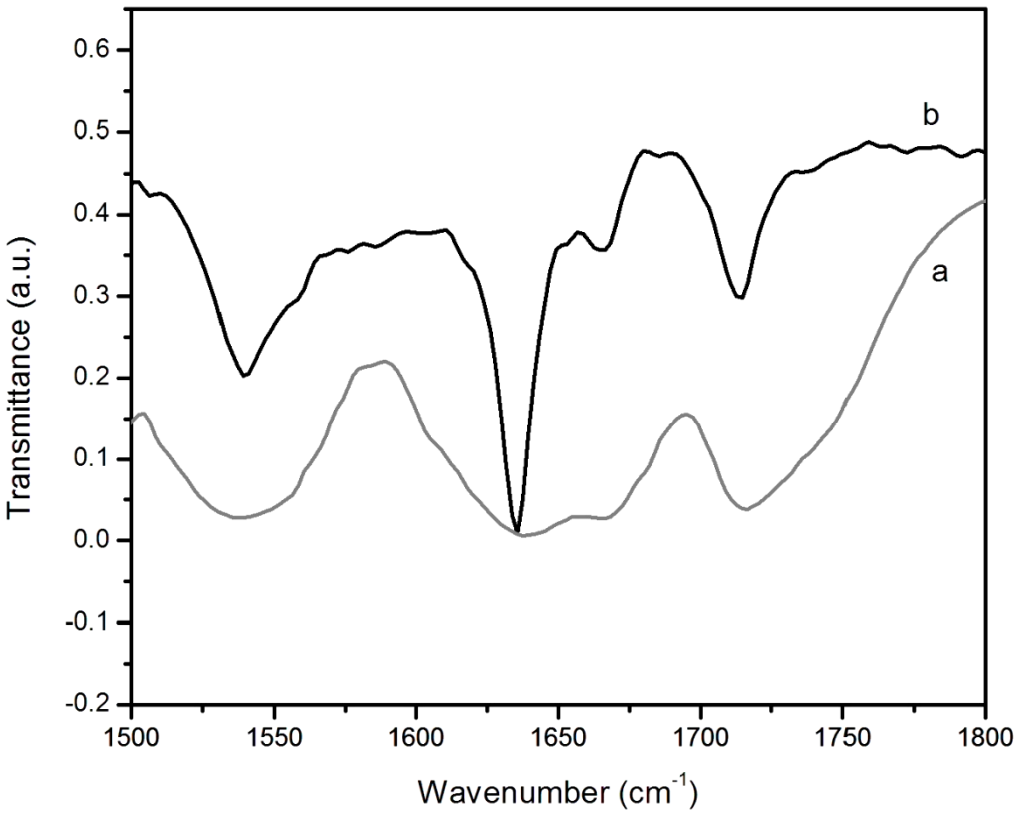
HO-Phe(4)-Val(3)-Suc-Leu(1)-Phe(2)-OH 3

1.63 g (2.5 mmol) of MeO-Phe(4)-Val(3)-Suc-Leu(1)-Phe(2)-OMe **12** in 150 ml MeOH was taken in a round bottom flask (R.B) and 2M NaOH was added to it dropwise. The reaction was monitored by thin layer chromatography (TLC). The reaction mixture was stirred for overnight. 15 ml of distilled water was added to the reaction mixture and MeOH was removed under vacuo. The aqueous part was washed with diethyl ether (2 x 30 ml). Then it was cooled under ice-water bath for 10 minute and then pH was adjusted to 1 by drop wise addition of 1M HCl. It was extracted with ethyl acetate (3 x 50 ml) and then the ethyl acetate part was dried over anhydrous Na_2SO_4 and evaporated in vacuo to yield **3** as a white solid. Yield: 1.43 g (2.3 mmol, 92%); R_f 0.4 ($CHCl_3$:CH_3OH:CH_3COOH = 10:2:0.1); FT - IR (KBr): ν = 3299 (s), 1717 (ms), 1639 (s), 1540 (s) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, δ): 8.13 - 8.11 (d, *J* = 7.2 Hz, 1H, NH- of Val (3)), 8.01 - 7.99 (d, *J* = 7.5 Hz, 1H, -NH of Leu (1)), 7.85 – 7.83 (d, *J* = 7.8 Hz, 1H, -NH of Phe (4)), 7.70 - 7.67 (d, *J* = 7.5 Hz, -NH of Phe (2)), 7.21 - 7.19 (m, 10 H, ring protons of Phe (2) and Phe (4)), 4.35 (m, 2H, C^{α}Hs of Phe (2) and Phe (4)), 4.24 (m,1H , C^{α}H of Leu(1)), 4.14 (m, 1H, C^{α}H of Val(3)), 3.01 - 2.98 and 2.91 - 2.88 (d, *J* = 9.3 Hz, *J* = 8.7 Hz, 4H , C^{β}Hs of Phe (2) and Phe (4)), 2.46 and 2.35 (m, 4H, -C$\underline{H}_2$- of Suc), 2.32 - 2.25 (m, 1H, C^{β}H of Val (3)), 1.88 - 1.83 (m, 2H, C^{β}Hs of Leu (1), 1H, C^{γ}H of Leu(1)), 0.79 - 0.77 (d, *J* = 6.6 Hz, 6H, C^{δ}Hs of Leu (1), 6H, C^{γ}Hs of Val (3)); ^{13}C NMR (75MHz , DMSO-

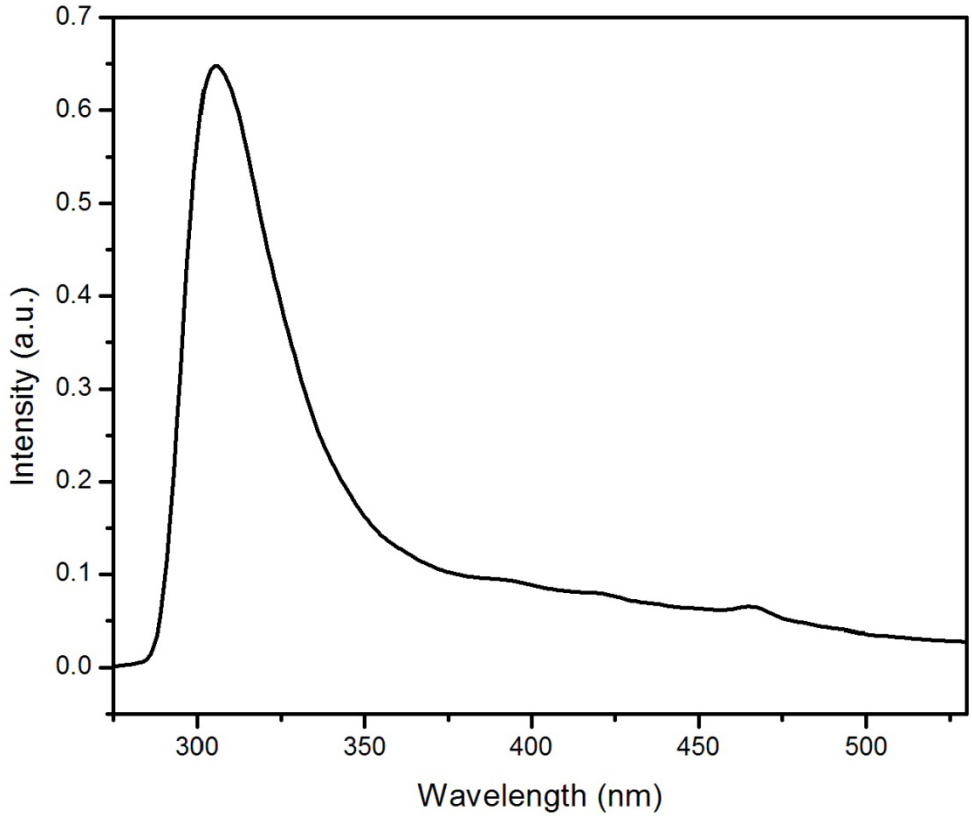
d_6 , δ_{ppm}): 173.03 (C=O), 172.34 (C=O), 171.52 (C=O), 171.32 (C=O), 162.07 (C=O), 137.74, 129.34, 129.30, 128.36, 127.28, 126.61, 57.50, 53.57, 50.91, 48.82, 40.99 ,40.47, 40.19, 39.91, 39.63, 39.36, 39.08, 38.80, 36.82, 31.11, 30.81, 24.27, 23.25, 21.81, 19.36; $[\alpha]_D^{20}$ = -28.06 (*c* = 0.5 in CH_3OH); ESI (*m/z* (%)): 624.2 (25) [M^+], 623.1 (100) [M^+ - H].



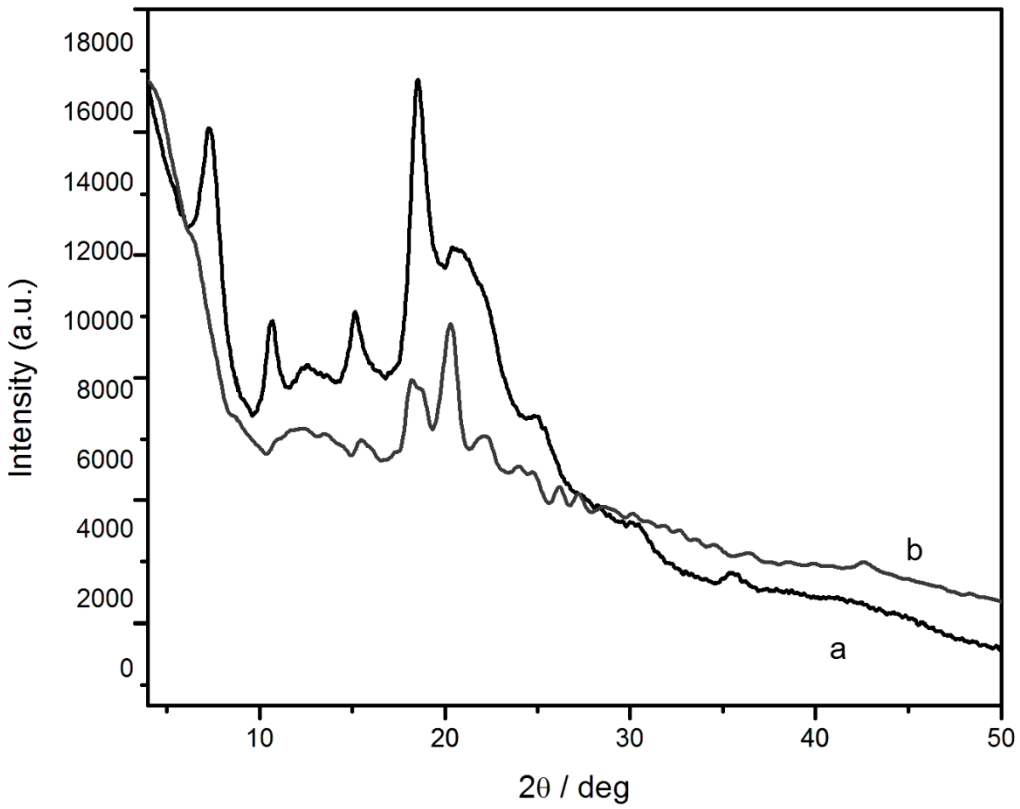
ESI Fig. 1. (a) Concentration dependence gelation temperature (T_{gel} / ^{0}C) of (a) the hydrogel of peptide bolaamphiphile **1,** (b) the hydrogel of peptide bolaamphiphiles **2** and (c) concentration-temperature phase diagram ln (φ) vs temp (K) of hydrogels **1** and **2**, where φ is the mole fraction and K is the temperature in Kelvin.



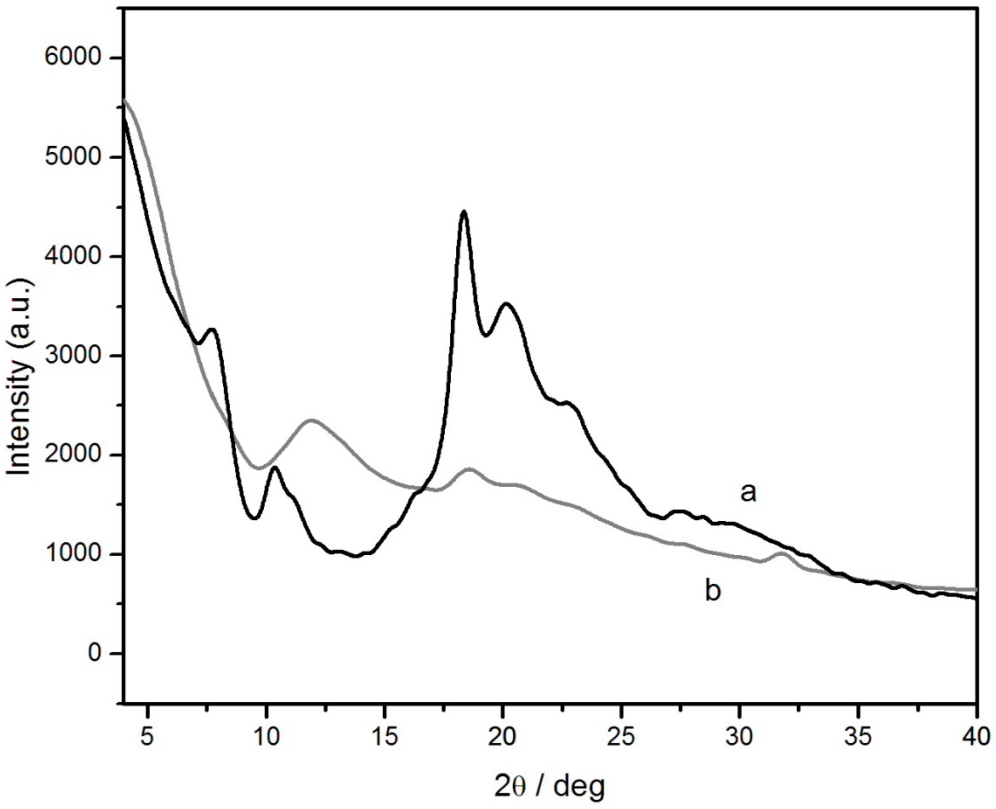
ESI Fig. 2. FT-IR spectra of (a) solid powder and (b) hydrogel of peptide bolaamphiphile **2.**



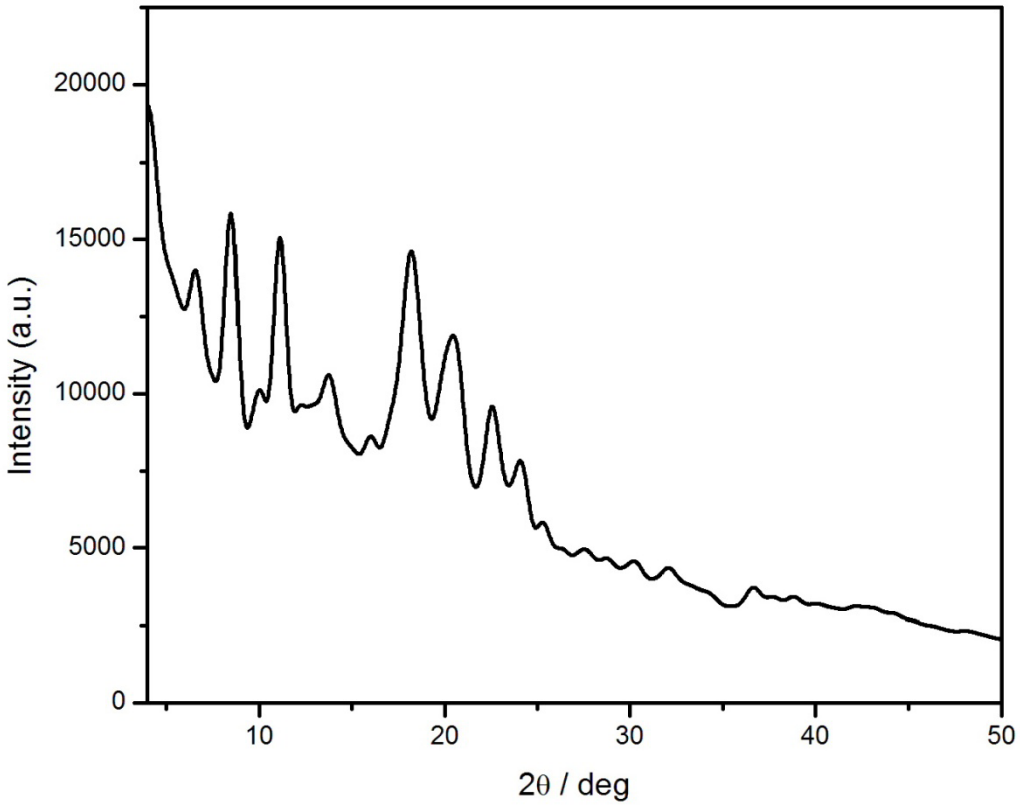
ESI Fig. 3. Fluorescence emission spectra of the hydrogel of peptide bolaamphiphile **1** (c = 20 mmol/liter, λ_{ex} = 276 nm, λ_{em} = 306 nm).



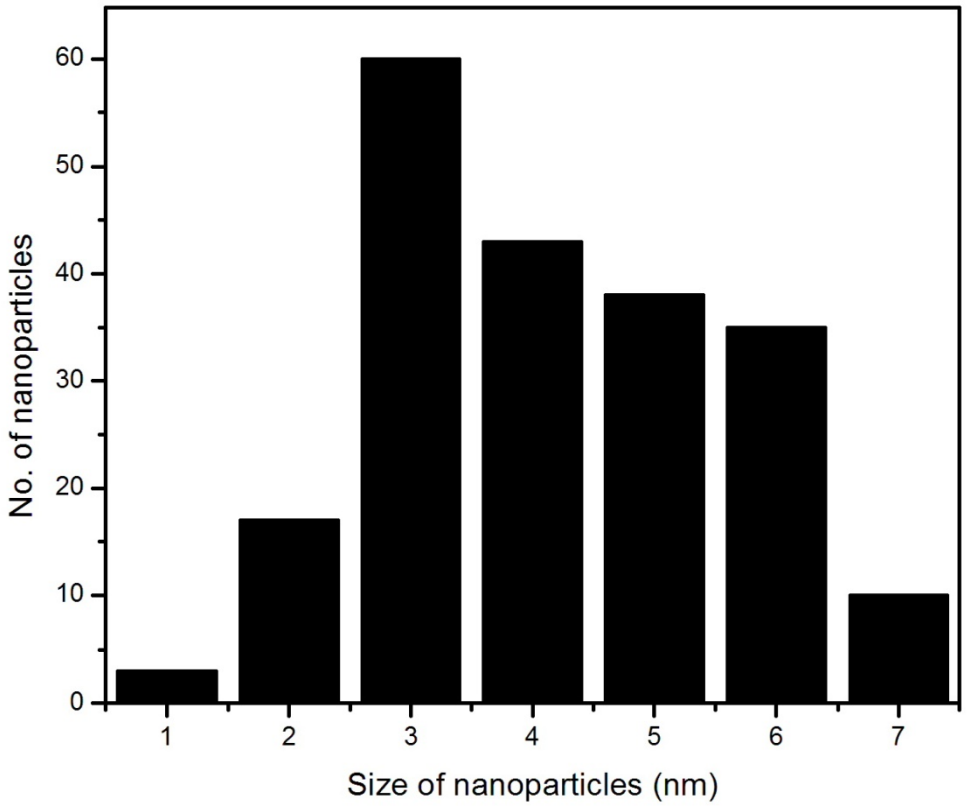
ESI Fig. 4. Wide angle powder XRD of (a) solid powder of peptide bolaamphiphile **1** and (b) it's dried hydrogel.



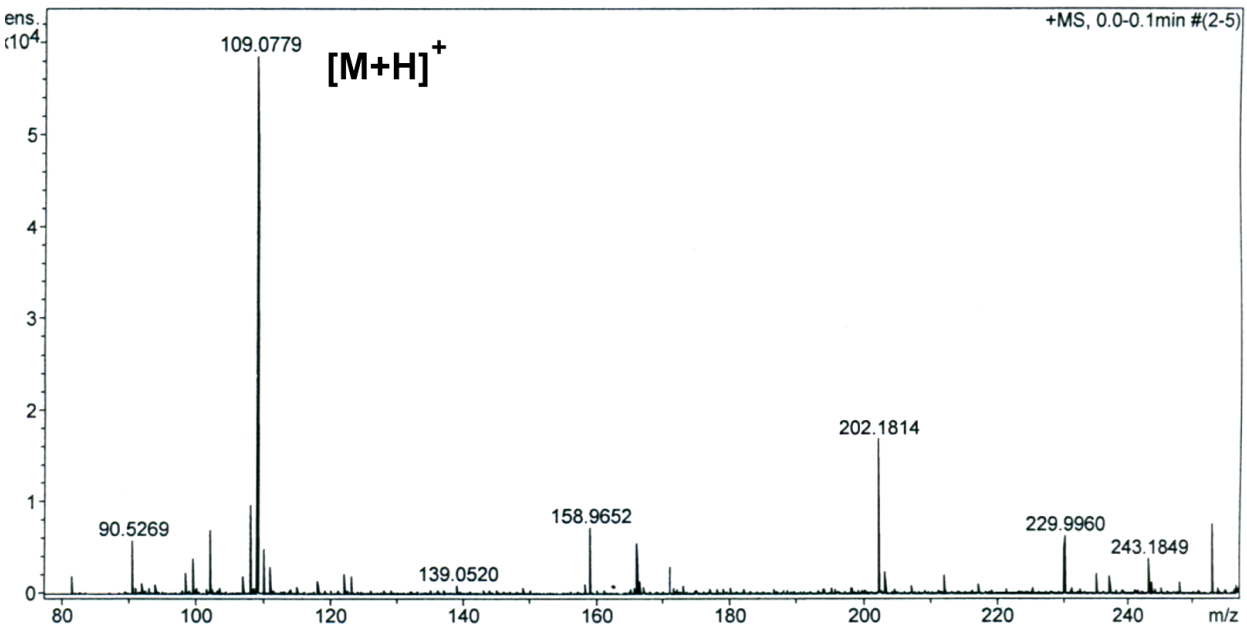
ESI Fig. 5. Wide angle powder XRD of (a) solid powder of peptide bolaamphiphile **2** and (b) it's dried hydrogel.



ESI Fig. 6. Wide angle powder XRD of solid powder of peptide bolaamphiphile **3** with numbers of sharp peaks indicating crystalline in nature.



ESI Fig. 7. The size distribution of Pt nanoparticles after 1 day of reaction time.



ESI Fig. 8: Mass spectra of Pt catalyzed hydrogenation of p-nitroaniline to p-phenylenediamine. The peak *m/z* $(M + H)^+$ = 109.0779 corresponds to synthesis of p-phenylenediamine.