Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Antara Dasgupta*

Department of Chemistry, IIT Guwahati
Guwahati, Assam - 781039
E-mail: dg.antara@iitg.ernet.in.

1- Peptide Synthesis

All the peptide amphiphiles (PAs) **1**-**7** were synthesized by solid phase peptide synthesis (SPPS) using Rink-amide MBHA resin and standard Fmoc synthesis protocol. The use of Rink-amide resin was to provide C-terminally amidated peptides in each case containing one lysine residue and the N-terminus with either one or two lipid chains or aromatic residues. After the deprotection of Rink-amide resin with a 20%-piperidine/DMF solution, Fmoc-Lys(Boc)-OH was introduced and coupled to the resin, followed by Fmoc deprotection and coupling of either Fmoc-Glu(OtBu)-OH/Fmoc-Lys(Boc)-OH/Fmoc-Lys(Fmoc)-OH depending on the sequence. The Fmoc deprotection and coupling was repeated twice/thrice until the designed peptide sequence was obtained in each case. After Fmoc deprotection of the N-terminal residue, one or two lipid chains or aromatic residue was finally coupled to N-terminal(s). All coupling reactions were affected by treatment with HBTU/HOBt/DIPEA. Fmoc deprotection reactions were carried out by using DMF solution containing piperidine (20%, v/v). Cleavage from the resin and deprotection of the protecting groups on the side-chains were performed concurrently with a mixture of TFA, DCM and H_2O at a ratio of 95:2.5:2.5. After rotary evaporation, the cleaved peptides were precipitated with cold diethyl ether, washed thrice with cold ether and then lyophilized.

^{1}H NMR, were recorded on a NMR-Bruker Ascend TM 600 MHz (Bruker, Coventry, UK). ESI-MS was performed by using a QTof Premier Quadrupole mass spectrometer.

2- MALDI-TOF-MS spectra of PAs1-7

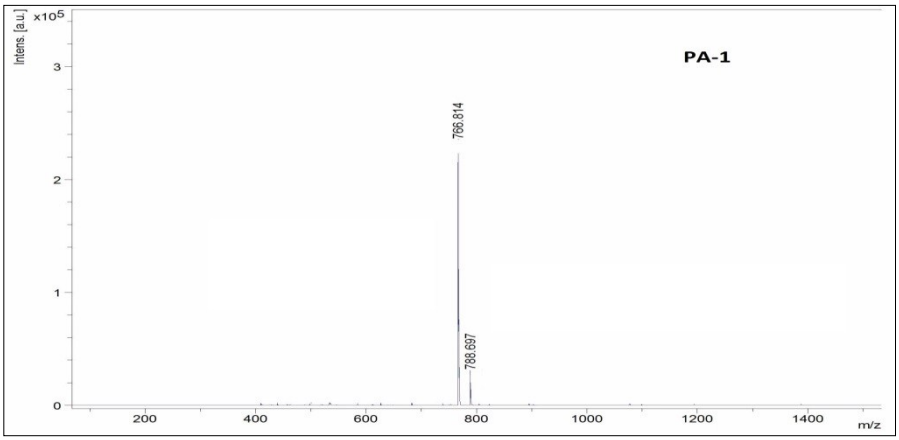

Fig. S1: Maldi spectra of PA-**1**

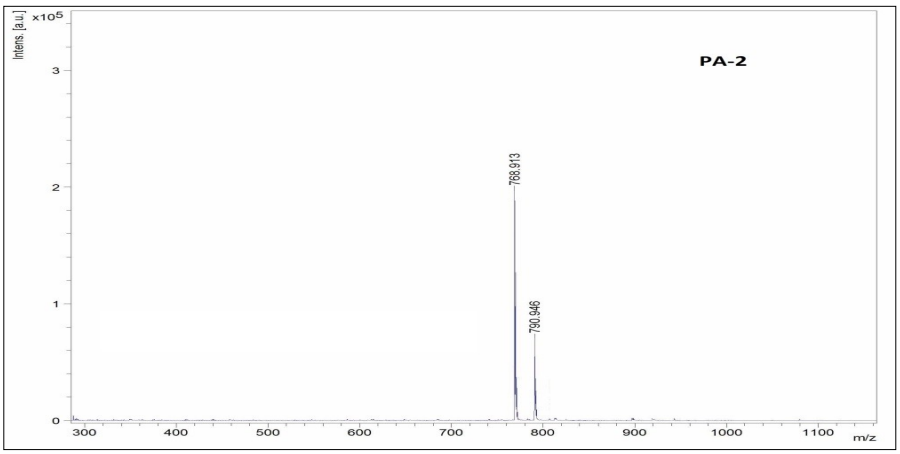

Fig. S2: Maldi spectra of PA-**2**

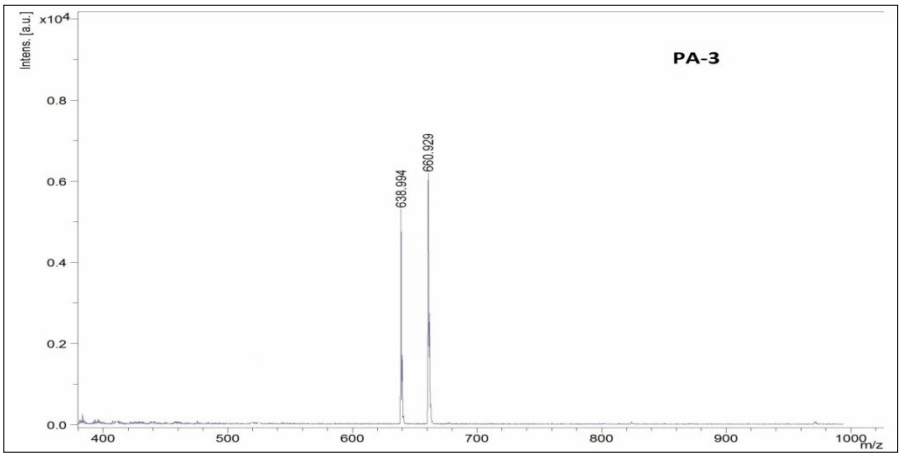

Fig. S3: Maldi spectra of PA-**3**

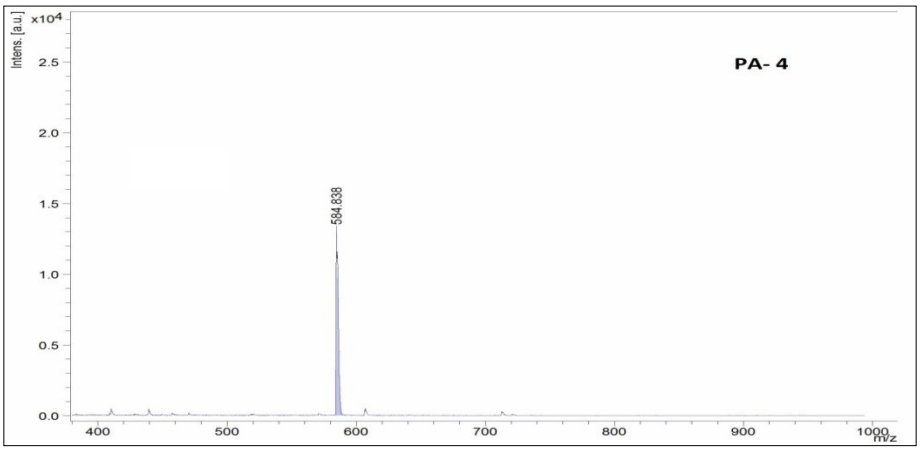

Fig. S4: Maldi spectra of PA-**4**

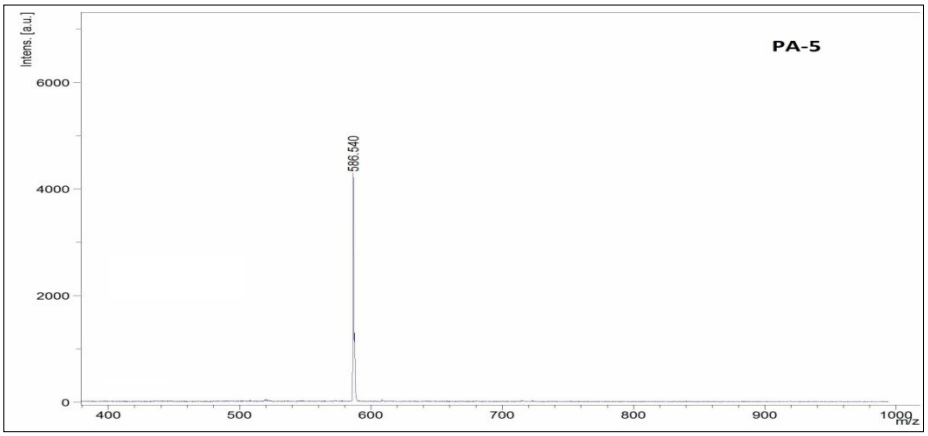

Fig. S5: Maldi spectra of PA-**5**

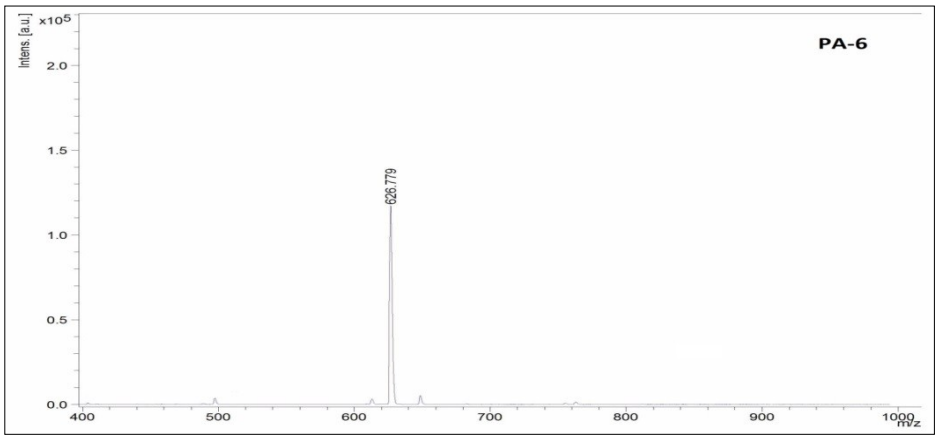

Fig. S6: Maldi spectra of PA-**6**

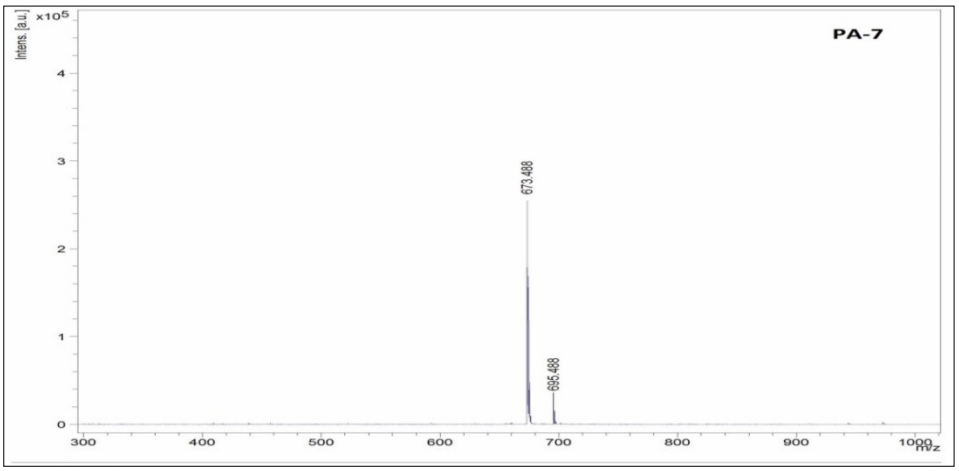

Fig. S7: Maldi spectra of PA-**7**

3 - **NMR characterisation data of PAs 1-7**

PA –**1**-^{1}H NMR (600 MHz, D_6-DMSO): δ = 0.84−0.86 (t, J = 6.0 Hz, 6H), 1.24 (br, 32H), 1.46 (br, 16H), 1.51 (br, 6H), 2.01-2.03 (br, 4H), 2.75 (br, 4H), 2.99 (br, 2H), 4.15 (br, 3H) 7.07 (NH, br, 1H), 7.36 (NH, br, 1H), 7.84 (NH, br, 1H), 7.95-7.97 (NH, t, J = 6 Hz, 1H), ppm; MS (ESI): m/z found $[M+H]^+$ 766.6532, expected 766.6456

PA – **2** -^{1}H NMR (600 MHz, D_6-DMSO): δ = 0.84−0.86 (t, J = 6.0 Hz, 6H), 1.23 (br, 32H), 1.46 (br, 12H), 1.51 (br, 4H), 1.79 (br, 2H), 2.01-2.03 (br, 4H), 2.74 (br, 4H), 2.99 (br, 2H), 4.15 (br ,3H) 7.07 (NH, br,1H), 7.30 (NH, br, 1H), 7.82 (NH,br, 1H), 7.96-7.98 (NH, t, J = 6.0 Hz, 1H), 12.15(-COOH, br, 1H)ppm; MS (ESI): m/z found $[M+H]^+$767.5802, expected 767.5932

PA – **3** - ^{1}H NMR (600 MHz, D_6-DMSO): δ = 0.84−0.86 (t, J = 6.0 Hz, 6H), 1.24 (br, 32H), 1.46 (br, 12H), 1.51 (br, 4H), 2.01-2.03 (br, 2H), 2.08-2.11 (m, 2H), 2.75 (br, 2H), 2.99 (br, 2H), 4.15 (br, 2H) 7.05 (NH, br, 1H), 7.29 (NH, br, 1H), 7.92 (NH, d, 1H), ppm; MS (ESI): m/z found $[M+H]^+$ 638.5653, expected 638.55

PA – **4** - ^{1}H NMR (600 MHz, D_6-DMSO): δ = 0.84−0.86 (t, J = 6.0 Hz, 3H), 1.22 (br, 18H), 1.49 (br, 12H), 1.62 (br, 6H), 2.10 (br, 2H), 2.73 (br, 6H), 4.11 (br, 3H), 7.04 (NH, br, 1H), 7.35 (NH,br, 1H), 7.94 (NH, d, 1H),ppm; MS (ESI): m/z found $[M+H]^+$ 584.487, expected 584.4785

PA – **5** -^{1}H NMR (600 MHz, D_6-DMSO): δ = 0.83-0.85 (t, J = 6.0 Hz, 3H), 1.22 (br, 18H), 1.50 (br, 8H), 1.63 (br, 4H), 1.73 (br, 2H), 2.10 (br, 2H),2.4 (br, 2H) 2.73 (br, 4H), 4.13 (m, 3H),

7.05 (NH, br, 1H), 7.26 (NH, br, 1H), 7.80 (NH, d, 1H), 12.15(-COOH, br, 1H)ppm; MS (ESI): m/z found $[M+H]^+$585.435, expected 585.4261

PA – **6** -^{1}H NMR (600 MHz, D_6-DMSO): δ =1.27 (br,4H), 1.49 (br, 4H), 1.62 (br, 2H), 1.77 (br, 2H), 1.89 (br, 2H), 2.23 (br, 4H), 2.73 (br, 4H), 3.88 (br, 1H), 3.96 (br, 2H), 4.21 (br, 1H), 4.28 (br, 2H), 7.05 (NH,br, 1H), 7.31 (m, 2H), 7.41 (m, 2H), 7.69 (m, 2H), 7.89 (m, 2H)), 12.15(-COOH, br, 1H) ppm; MS (ESI): m/z found $[M+H]^+$625.34, expected 625.33

PA – **7** - ^{1}H NMR (600 MHz, D_6-DMSO): δ = 1.25 (br, 4H), 1.50 (br, 4H), 1.63 (br, 2H), 1.73 (br, 2H), 1.89 (br, 2H), 2.00 (br, 2H), 2.26 (m, 4H), 2.73 (br, 4H), 3.33 (m, 2H), 4.10 (br, 2H), 4.34 (br, 1H), 7.06 (NH, br, 1H), 7.34 (NH, br, 1H), 7.75 (NH, br, 1H), 7.84 (d, J=6 Hz, 1H), 7.94 (d, J=6 Hz, 2H), 8.05 (m, 3H), 8.19 (m, 2H), 8.36 (d, J=6 Hz, 1H), 12.15 (-COOH, br, 1H) ppm; MS (ESI): m/z found $[M+H]^+$ 673.4, expected 673.36.

4. Temperature dependent ^{1}H-NMR study of PA-2 hydrogels

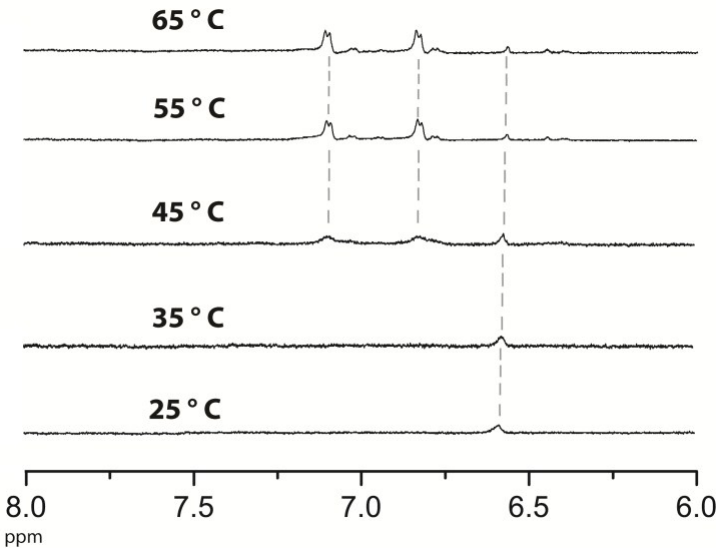

Fig. S8: ^{1}H-NMR spectra of PA-**2**(2 wt%) in 50% [D_6]DMSO/50% D_2O with increasing temperature

5. Rheology

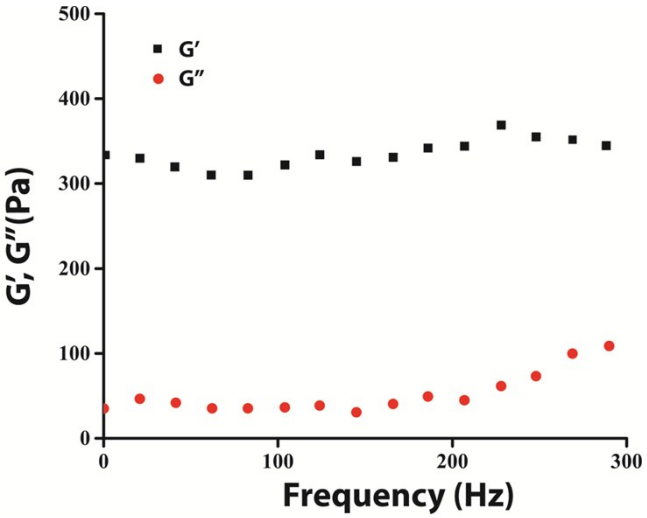

Fig. S9: Elastic Modulus of PA-**2** hydrogel

6. EDX spectrum of mineralized calcium phosphate in hydrogels of PA-3

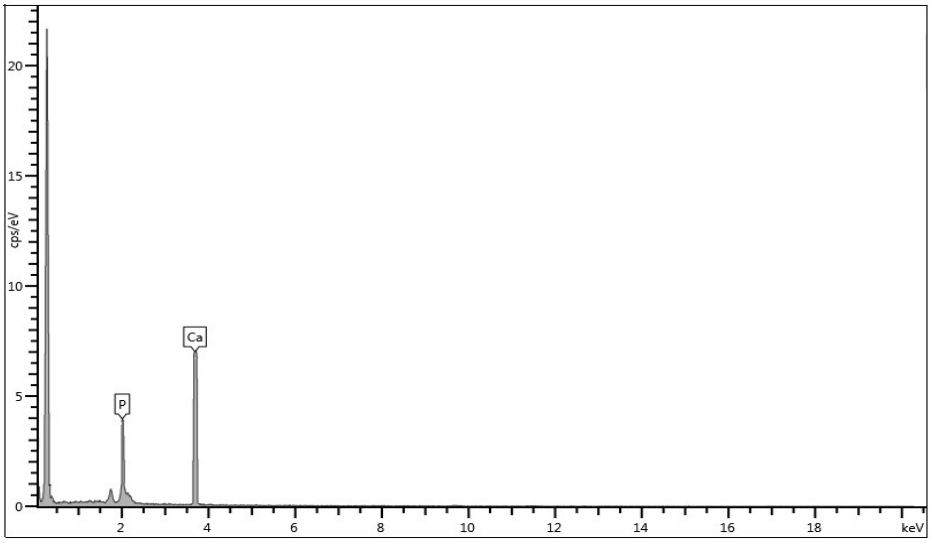

Fig. S10: Energy dispersive X-ray analysis of hybrid nanofibers obtained from the hydrogels of PA - **3** in FESEM observation after calcium phosphate biomineralization