Supporting Information

Metal-Ion Modulated Structural Transformation of Amyloid-Like Dipeptide Supramolecular Self-Assembly

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Materials: All the solvents and chemicals are commercially available. Chemicals were used without further purification. Water was processed using a Millipore purification system (Darmstadt, Germany) with a minimum resistivity of 18.2 MΩ cm. Sodium chloride, potassium chloride, zinc chloride, copper (II) chloride, iron (III) chloride, and aluminum chloride were purchased from Sigma, and ultrapure water was obtained from Biological Industries. Fmoc-modified diphenylalanine (FmocFF) was purchased from Bachem at a purity level of >98%.

NMR: ^{1}H and ^{13}C NMR spectra were recorded in deuterated solvent on a Bruker Advance 400 MHz spectrometer. The ^{1}H NMR chemical shifts (δ) are given in ppm, referring to internal standard tetramethylsilane (TMS). All coupling constants (*J*) are given in Hz. FmocFF: ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.67 (s, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 4.0 Hz, 2H), 7.48-7.57 (m, 3H), 7.31-7.34 (m, 2H), 7.08-7.21 (m, 12H), 4.38-4.43 (m, 1H), 4.17-4.23 (m, 1H), 4.01-4.08 (m, 3H), 2.99-3.03 (dd, J_1 = 4.0 Hz, J_1 = 12.0 Hz, 1H), 2.85-2.92 (m, 1H), 2.60-2.69 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 173.0, 171.9, 156.0, 144.1, 144.0, 140.9, 138.4, 137.6, 129.5, 129.4, 128.5, 128.3, 127.9, 127.3, 126.7, 126.5, 125.7, 125.6, 120.4, 66.7, 65.9, 56.28, 53.79, 46.88, 37.3, 37.0, 23.1. MS (ESI) calcd for $C_{33}H_{30}N_2O_5$ $[M+H]^+$, 535.2; found, 535.6.

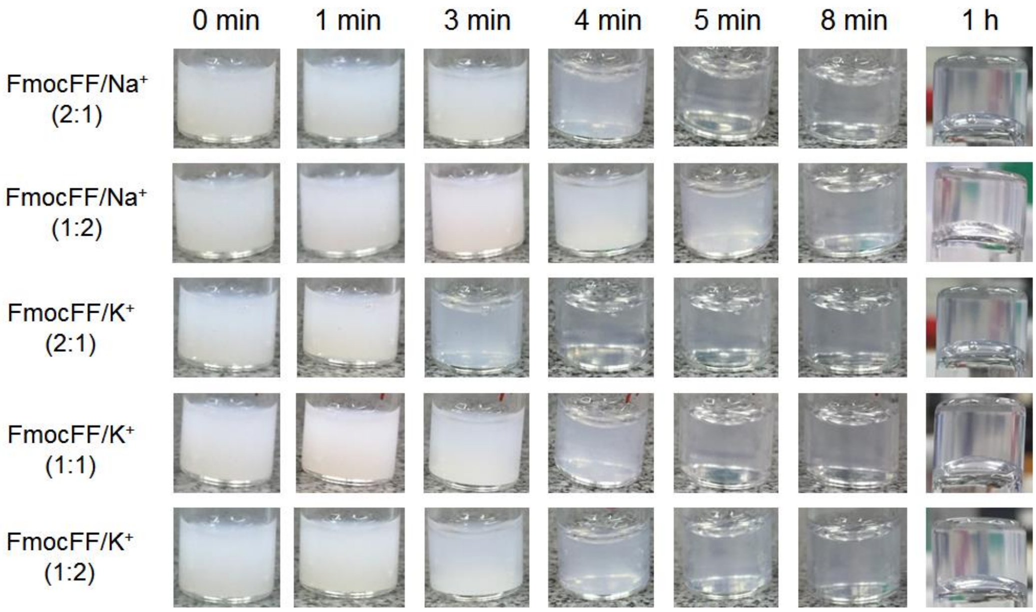

Figure S1. Time lapse images of FmocFF/Na^+ and FmocFF/K^+ at various molar ratios (2:1, 1:1, 1:2) in 2% DMSO in H_2O (v/v).

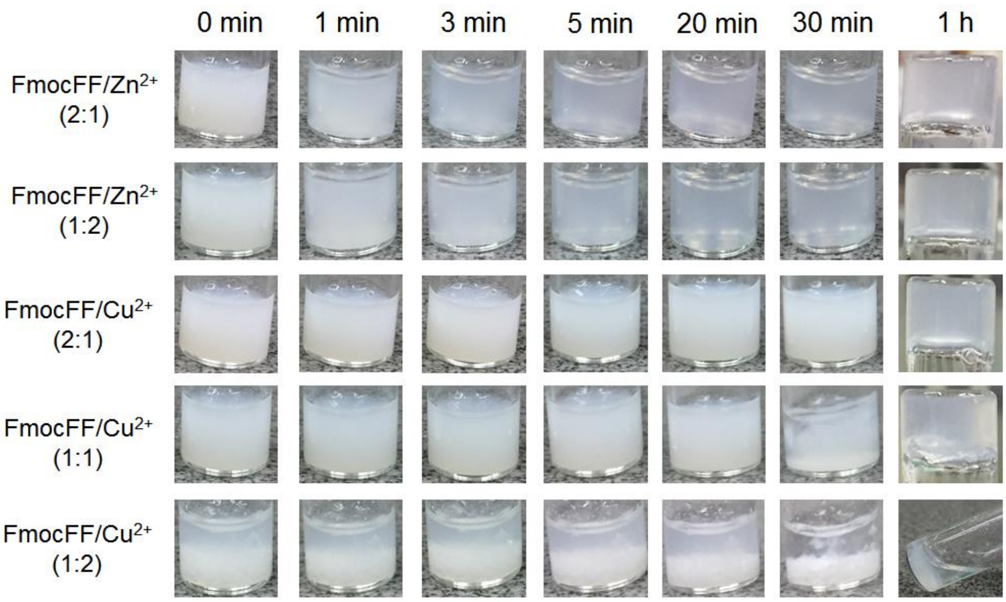

Figure S2. Time lapse images of FmocFF/Zn^{2+} and FmocFF/Cu^{2+} at various molar ratios (2:1, 1:1, 1:2) in 2% DMSO in H_2O (v/v). The FmocFF/Zn^{2+} (1:2) can form gel but not for FmocFF/Cu^{2+} (1:2), which may be ascribed to the good binding ability of Zn^{2+} with water molecules.[1] In addition, the size of FmocFF/Zn^{2+} compact fibrils are smaller that benefit the hydrogelation.

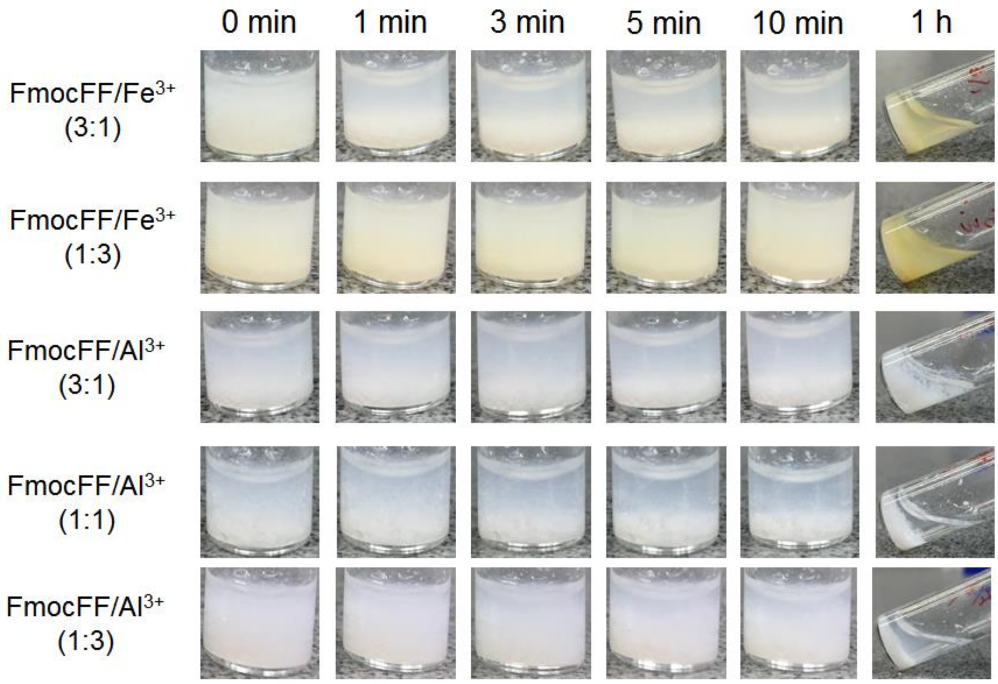

Figure S3. Time lapse images of FmocFF/Fe^{3+} and FmocFF/Al^{3+} at various molar ratios (3:1, 1:1, 1:3) in 2% DMSO in H_2O (v/v).

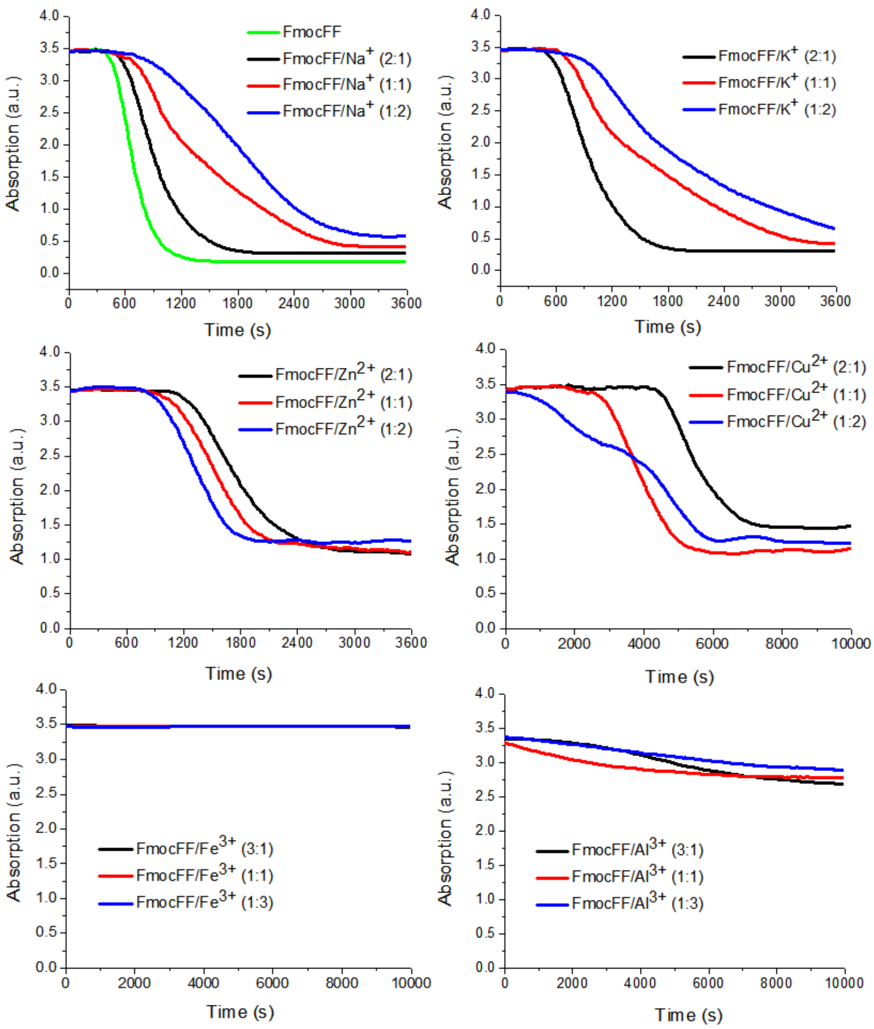

Figure S4. Turbidity measured at 405 nm over time for FmocFF and FmocFF/metal ions solutions in 2% DMSO in H_2O (v/v).

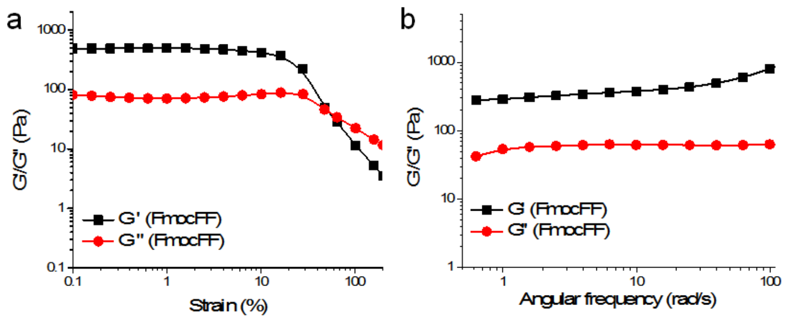

Figure S5. (a) Rheological measurements of strain sweep of the FmocFF hydrogel at a constant frequency of 1 Hz. (b) Rheological measurements of dynamic frequency sweep of the FmocFF hydrogel at a strain of 0.1% over a range of 0.1-100 rads^{-1}.

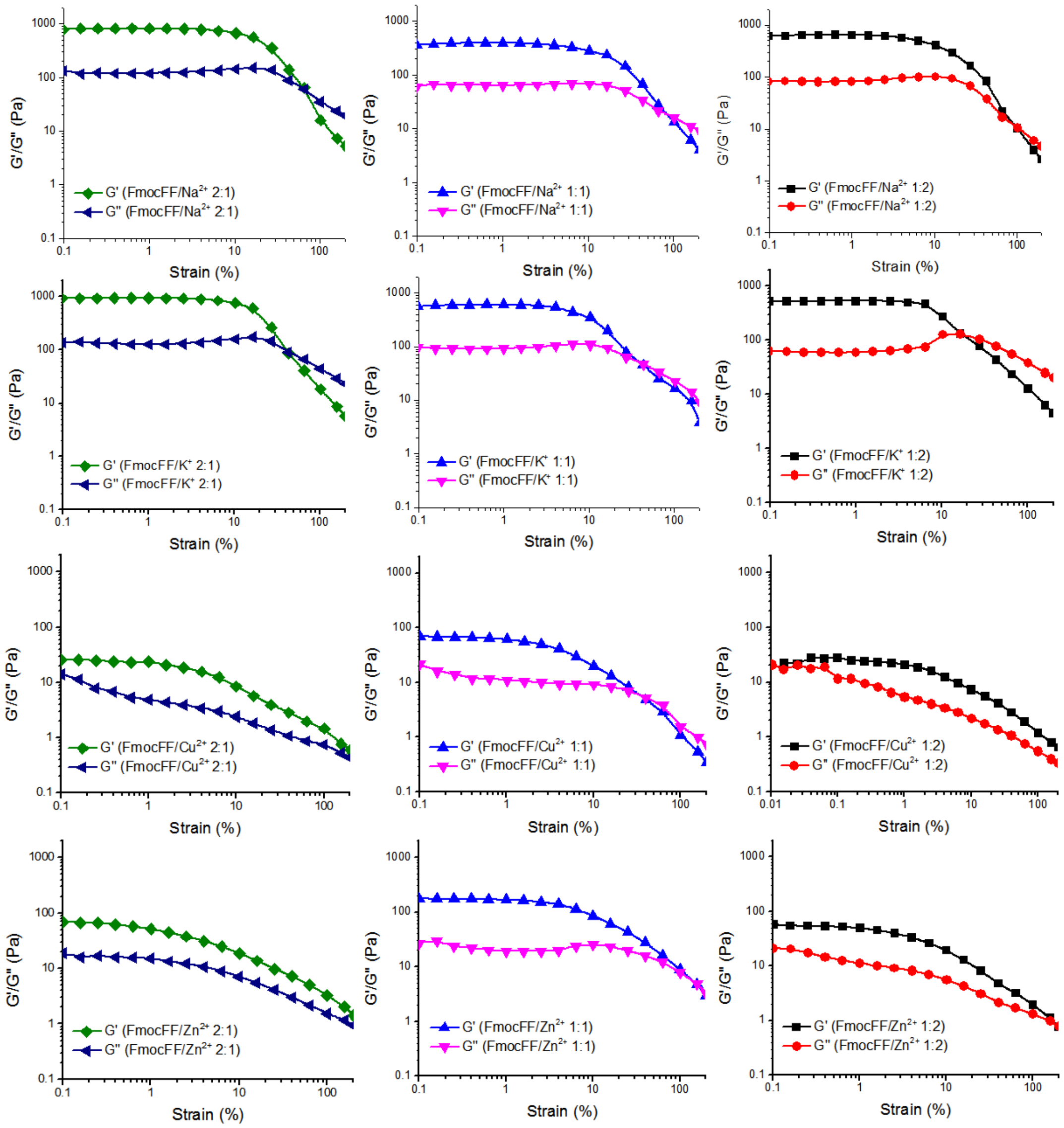

Figure S6. Rheological strain sweep measurements of different metallohydrogels at a constant frequency of 1 Hz.

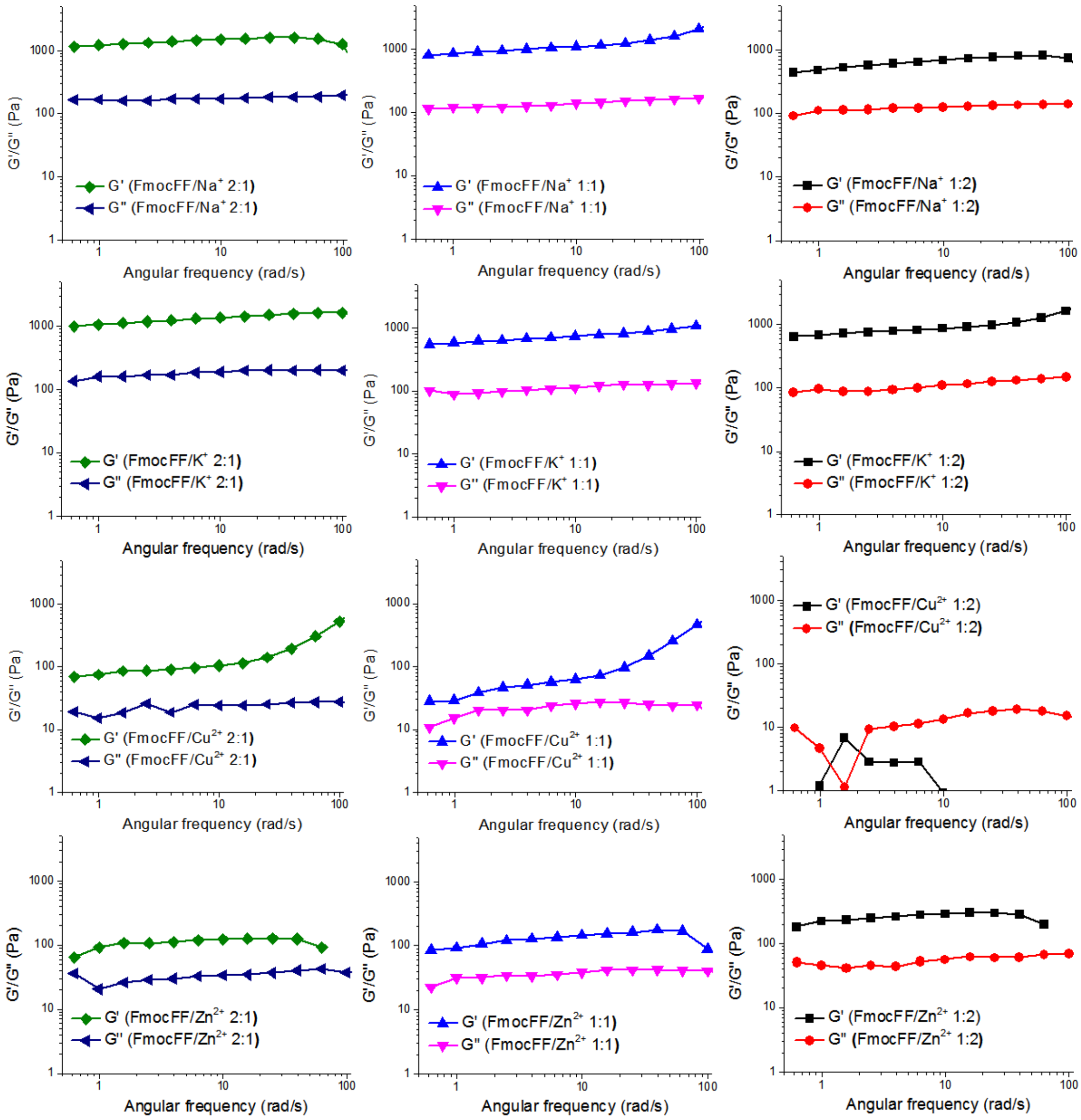

Figure S7. Rheological dynamic frequency sweep measurements of different metallohydrogels at a strain of 0.1% over a range of 0.1-100 rads^{-1}.

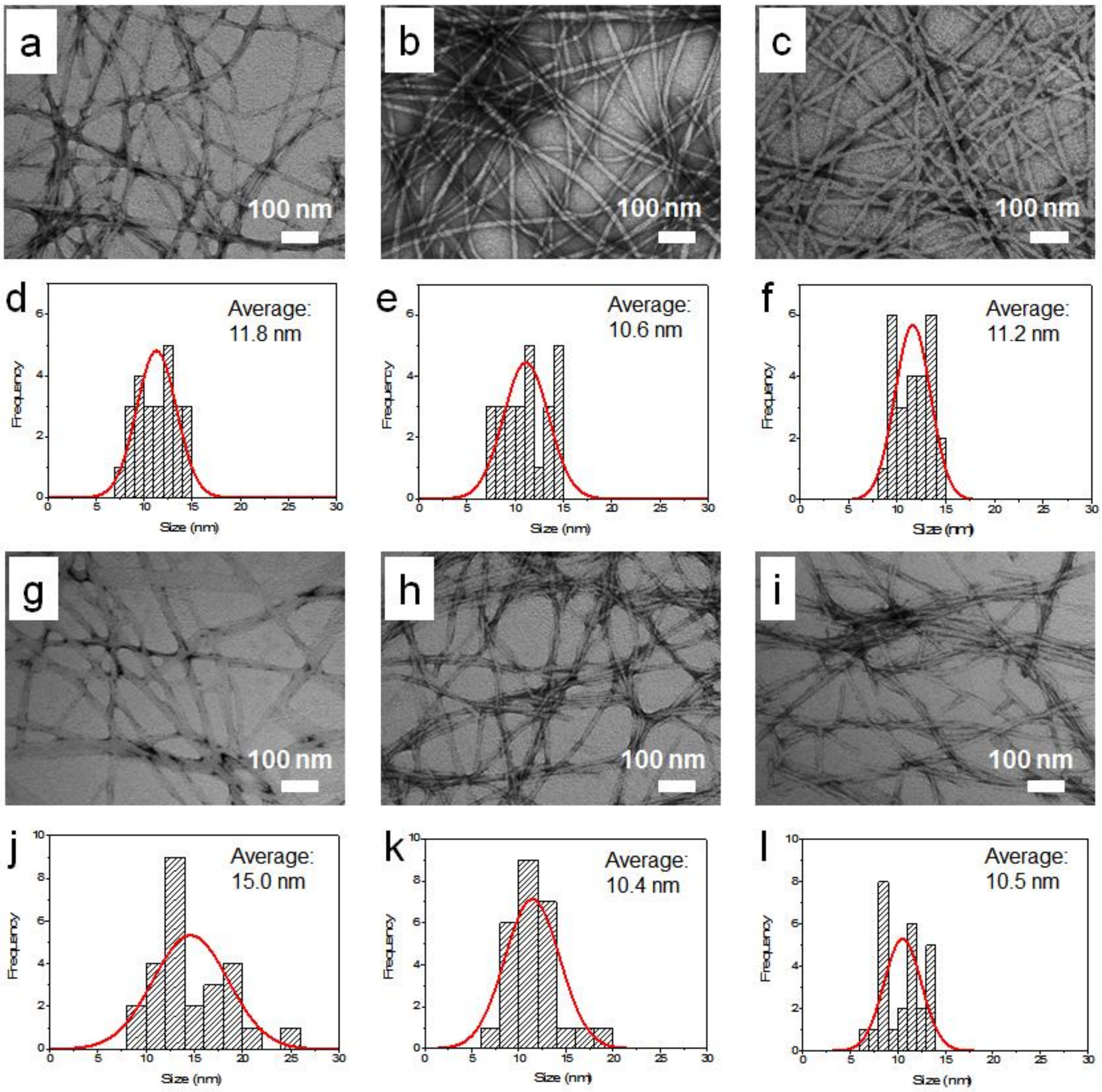

Figure S8. (a-c, g-i) TEM images and (d-f, j-l) average size distribution histogram of (a, d) FmocFF/Na^+ (2:1), (b, e) FmocFF/Na^+ (1:1), (c, f) FmocFF/Na^+ (1:2), (g, j) FmocFF/K^+ (2:1), (h, k) FmocFF/K^+ (1:1), and (i, l) FmocFF/K^+ (1:2) in 2% DMSO in H_2O (v/v) at a concentration of 2 mg/mL. Scale bar is 100 nm.

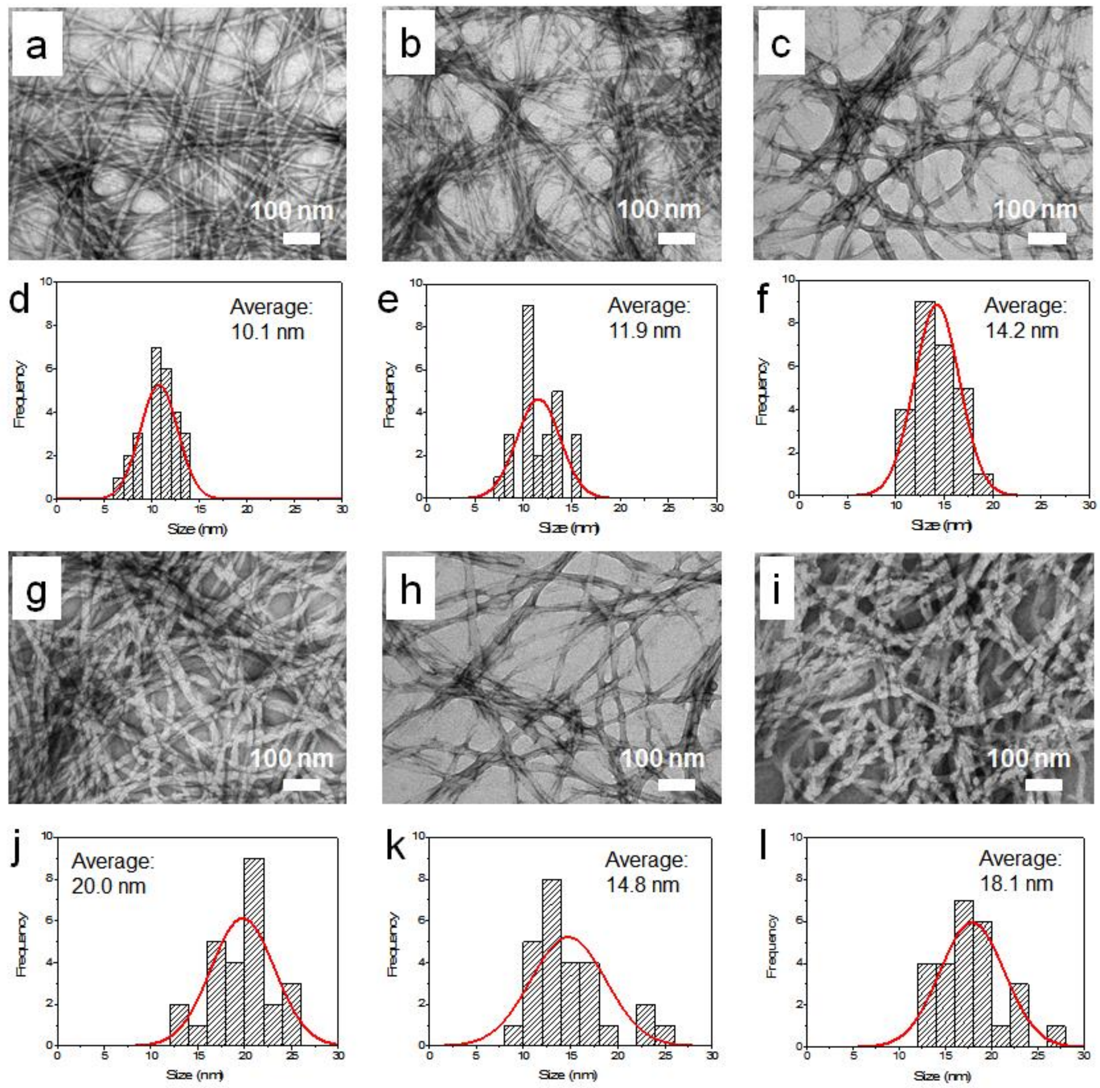

Figure S9. (a-c, g-i) TEM images and (d-f, j-l) average size distribution histogram of (a, d) FmocFF/Zn^{2+} (2:1), (b, e) FmocFF/Zn^{2+} (1:1), (c, f) FmocFF/Zn^{2+} (1:2), (g, j) FmocFF/Cu^{2+} (2:1), (h, k) FmocFF/Cu^{2+} (1:1), and (i, l) FmocFF/Cu^{2+} (1:2) in 2% DMSO in H_2O (v/v) at a concentration of 2 mg/mL. Scale bar is 100 nm.

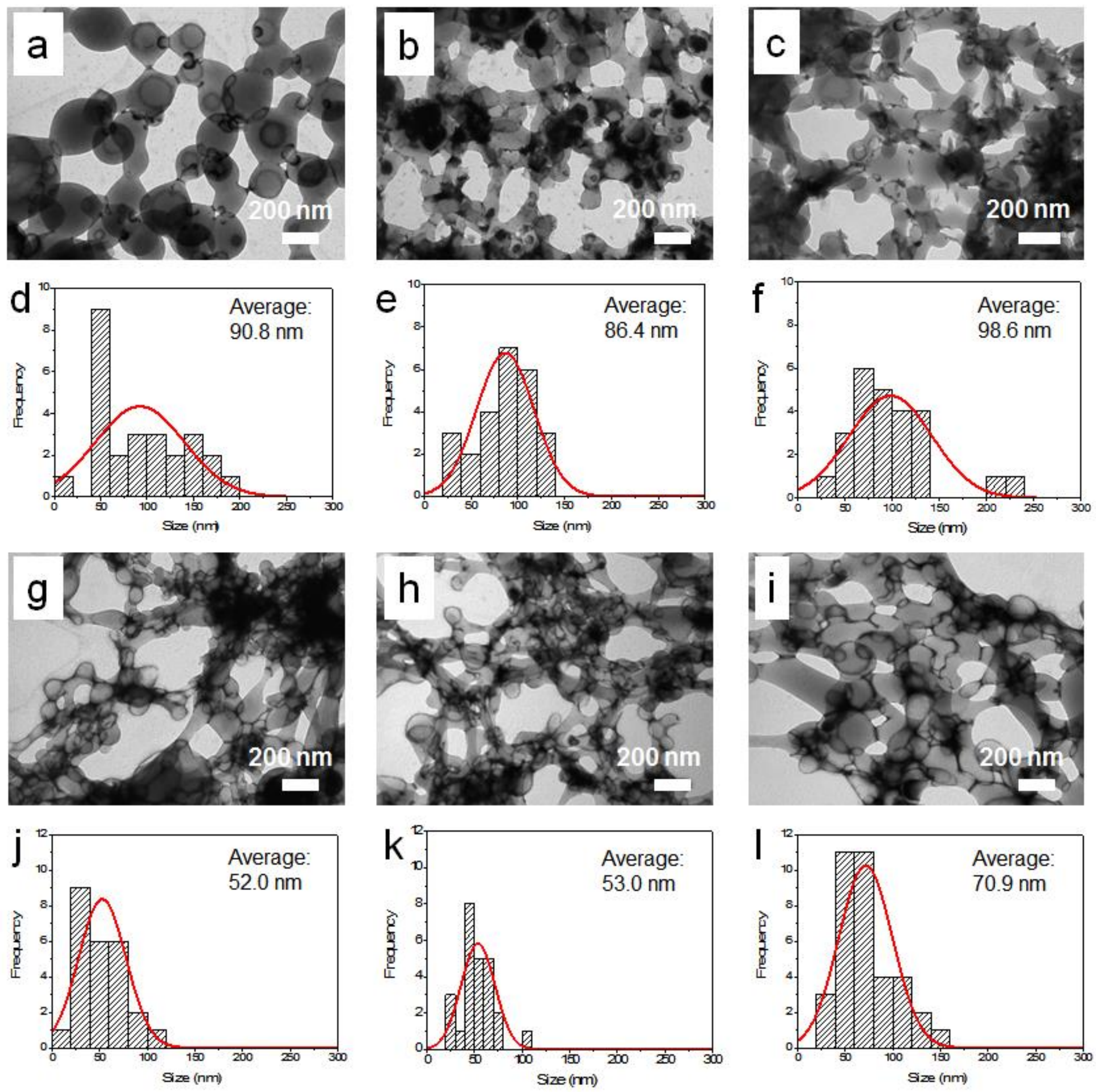

Figure S10. (a-c, g-i) TEM images and (d-f, j-l) average size distribution histogram of (a, d) FmocFF/Fe^{3+} (3:1), (b, e) FmocFF/Fe^{3+} (1:1), (c, f) FmocFF/Fe^{3+} (1:3), (g, j) FmocFF/Al^{3+} (3:1), (h, k) FmocFF/Al^{3+} (1:1), and (i, l) FmocFF/Al^{3+} (1:3) in 2% DMSO H_2O (v/v) at a concentration of 2 mg/mL. Scale bar is 200 nm.

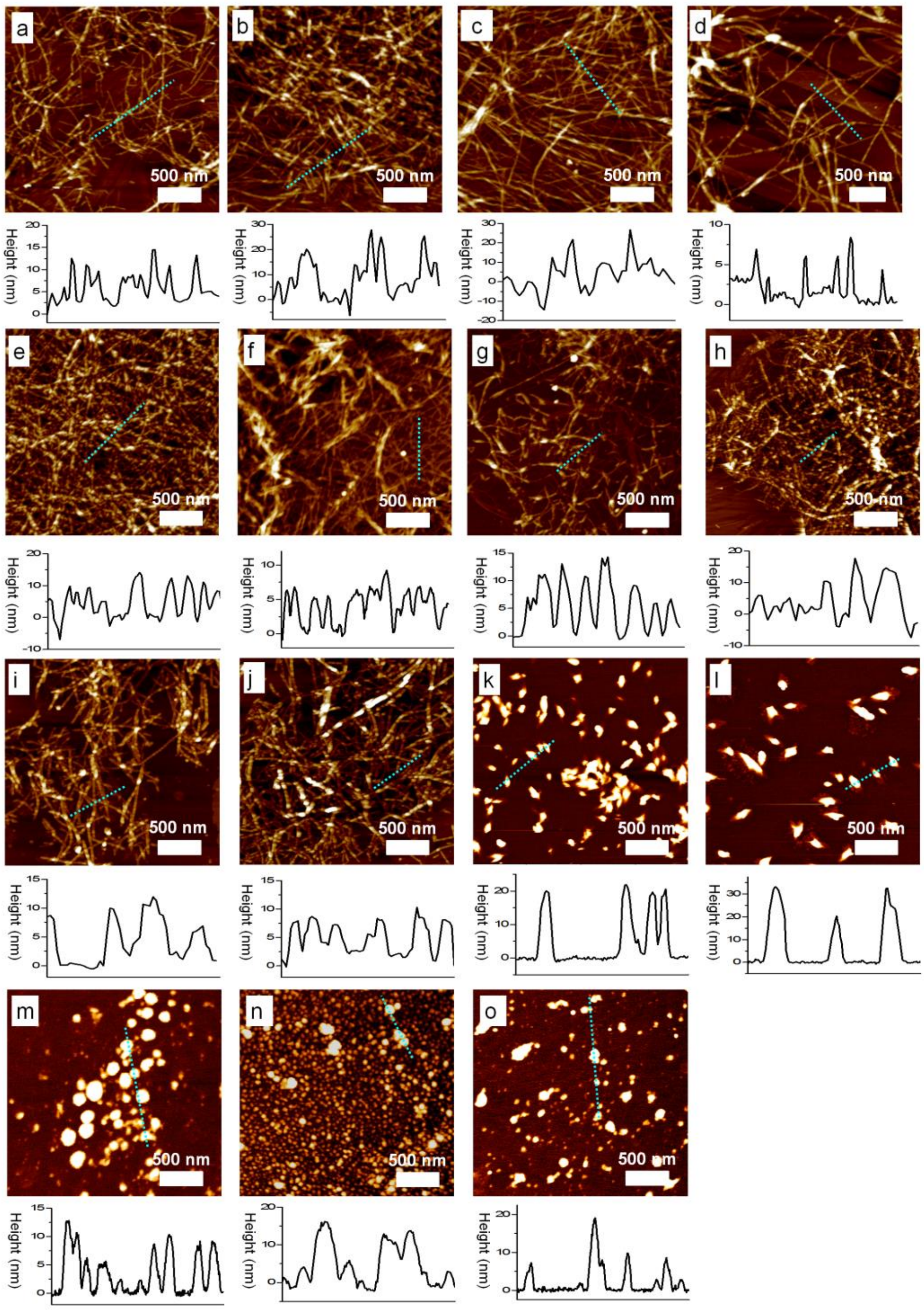

Figure S11. AFM images (top) and height distribution (bottom) of (a) FmocFF/Na^{+} (2:1), (b) FmocFF/Na^{+} (1:2), (c) FmocFF/K^{+} (2:1), (d) FmocFF/K^{+} (1:1), (e) FmocFF/K^{+} (1:2), (f) FmocFF/Zn^{2+} (2:1), (g) FmocFF/Zn^{2+} (1:2), (h) FmocFF/Cu^{2+} (2:1), (i) FmocFF/Cu^{2+} (1:1), (j) FmocFF/Cu^{2+} (1:2), (k) FmocFF/Fe^{3+} (3:1), (l) FmocFF/Fe^{3+} (1:3), (m) FmocFF/Al^{3+} (3:1), (n) FmocFF/Al^{3+} (1:1), and (0) FmocFF/Al^{3+} (1:3) in 2% DMSO in H_2O (v/v) at a concentration of 2 mg/mL. Scale bar is 500 nm.

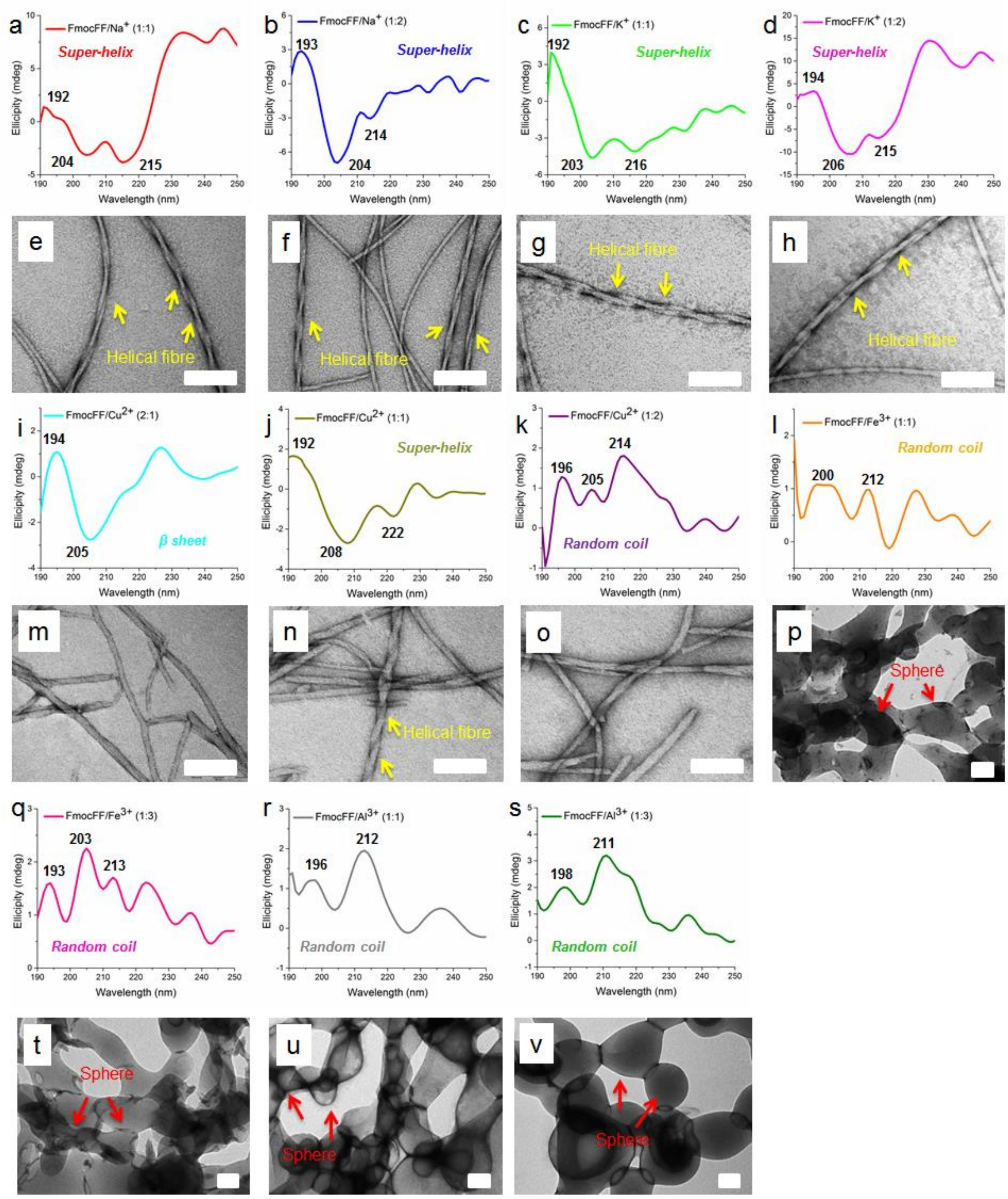

Figure S12. (a-d, i-l, q-s) CD spectra and e-h, m-p, t-v) high-resolution TEM images of FmocFF with different metal ions in 2% DMSO in H_2O (v/v) at a concentration of 2 mg/mL. (a, e) FmocFF/Na^+ (1:1), (b, f) FmocFF/Na^+ (1:2), (c, g) FmocFF/K^+ (1:1), (d, h) FmocFF/K^+ (1:2), (i, m) FmocFF/Cu^{2+} (2:1), (j, n) FmocFF/Cu^{2+} (1:1), (k, o) FmocFF/Cu^{2+} (1:2), (l, p) FmocFF/Fe^{3+} (1:1), (q, t) FmocFF/Fe^{3+} (1:3), (r, u) FmocFF/Al^{3+} (1:1), and (s, v) FmocFF/Al^{3+} (1:3). Scale bar is 50 nm.

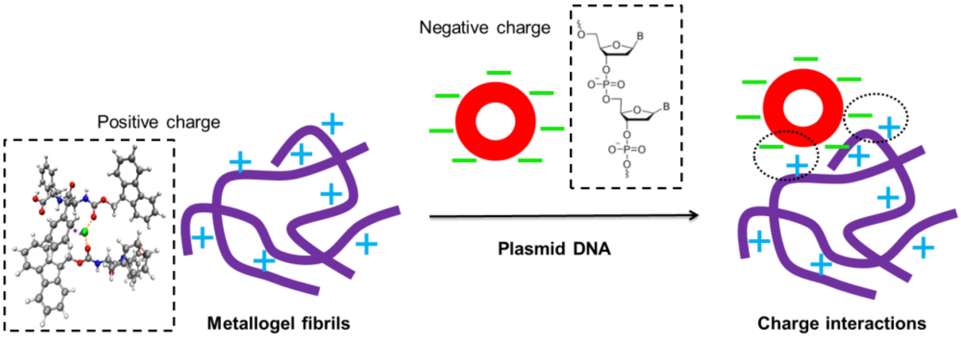

Figure S13 The electrostatic interactions between positively charged metallogel fibrils and negatively charged plasmid DNA.

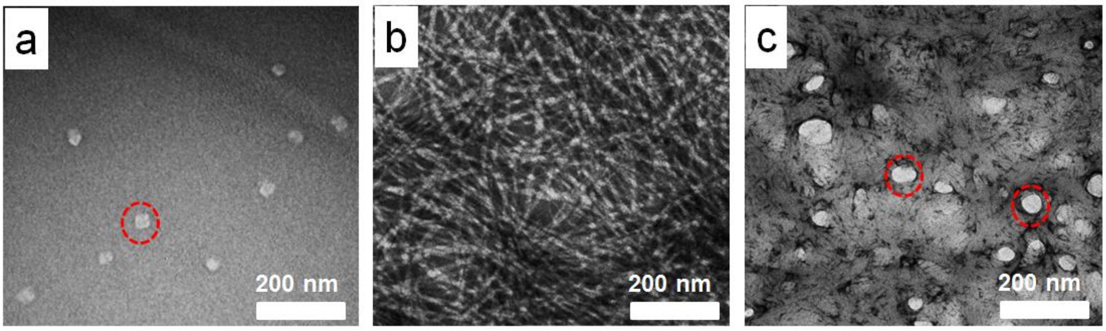

Figure S14 (a) TEM image of plasmid DNA. (b-c) TEM images of DNA binding to the (b) FmocFF and (c) FmocFF/Zn^{2+} 1:1 hydrogels after addition of DNA for 0.5 hour. Scale bar is 200 nm.

Reference

1. Hartmann, M.; Clark, Timothy.; Eldik, R. Hydration and Water Exchange of Zinc(II) Ions. Application of Density Functional Theory. *J. Am. Chem. Soc.* **1997**, *119*, 7843-7850.