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Influence of chiral ligand on the gel formation of a Mg(II) coordination polymer

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Supporting information

S1 Instrumentation

All starting materials were obtained commercially and used as received. The elemental analyses were performed in the microanalytical laboratory, Department of Chemistry, National University of Singapore. ^{1}H NMR spectra were recorded on a Bruker ACF 300 spectrometer operating in the quadrature mode at 300 MHz. The infrared spectra (KBr pellet) were recorded using an FTS165 Bio−Rad FTIR spectrophotometer in the range of 400−4000 cm^{-1}. Electrospray Ionization (ESI) mass spectra were recorded on a Finnigan MAT LCQ mass spectrometer using syringe pump method. High resolution ESI mass spectra were obtained on a Shimadzu LCMS-IT-TOF spectrometer including an SPD-M20A prominence PDA detector, CBM-20A prominence communication bus module, CTO-20A prominence column oven, SIL-20AC prominence auto sampler, DGU-20A3 prominence degasser and LC-20AD prominence liquid chromatograph. Shimadzu Formula Predictor Software was used to process the data. MS and HRMS were reported in units of mass of charge ratio (m/z). Solvent present in the compounds was determined using an SDT 2960 TGA thermal analyzer with a heating rate of 5°C min^{-1} from room temperature to 600°C. Scanning electron microscopy (SEM) images were taken using a Jeol JSM−6700F field emission scanning electron microscope operated at 5 kV and 10 μA. The fluorescence spectra were obtained from Perkin−Elmer LS 55 luminescence spectrometer. Dynamic oscillation strain and frequency sweeps were carried out on freshly prepared samples using a controlled stress rheometer (AR−1000N, TA Instruments Ltd., New Castle, DE, USA). Parallel plate geometry of 40 mm diameter and 1.5 mm gap was employed throughout. Following loading, the exposed edges of samples were covered with a silicone fluid from BDH (100 cs) to prevent water loss.

S2 Synthesis and characterization

Synthesis of ligands: A warm solution of 4-methylumbelliferrone (0.881 g, 5 mmol) in ethanol (30 mL) was treated with *D*- or *DL*-alanine (0.445 g, 5 mmol) in water (20 mL) and formaldehyde (37%, 370 μL, 5 mmol). The reaction mixture was heated at 90°C for 8 hours. The resulting precipitate was filtered off and recrystallized using 1:1 water:ethanol solution. Synthesis and characterization of *N*-(7-hydroxy-4-methyl-8-

coumarinyl)-*L*-alanine, *L*-H_2muala (**1a**) and hydrogel [Mg(*L*-muala)(H_2O)$_2$]·*n*H_2O (**2**) can be found in our previous studies.[1]

N-(7-hydroxy-4-methyl-8-coumarinyl)-*D*-alanine, *D*-H_2muala

Yield: 0.76 g, (55 %). Anal. Calcd. for $C_{14}H_{15}NO_5$ (277.28): C, 60.64; H, 5.45; N, 5.05; found: C, 60.36; H, 5.37; N, 5.07. ^{1}H NMR (D_2O, ppm): δ 7.48 (d, 1H, Ar), 6.71 (d, 1H, Ar), 5.85 (s, 1H, Ar), 3.84 (q, 2H, -CH_2N), 3.24 (q, 1H, -CH-Me), 2.40 (s, 3H, -ArCH_3), 1.25 (d, 3H, -CH_3).

N-(7-hydroxy-4-methyl-8-coumarinyl)-*DL*-alanine, *DL*-H_2muala

Yield: 0.87 g, (63 %). Anal. Calcd. for $C_{14}H_{15}NO_5$ (277.28): C, 60.64; H, 5.45; N, 5.05; found: C, 60.23; H, 5.40; N, 5.06. ^{1}H NMR (D_2O, ppm): δ 7.44 (d, 1H, Ar), 6.64 (d, 1H, Ar), 5.90 (s, 1H, Ar), 3.81 (s, 2H, -CH_2NH), 3.20 (q, 1H, -CH-Me), 2.36 (s, 3H, -ArCH_3), 1.22 (d, 3H, -CH_3).

Synthesis of fiber [Mg(*D*-muala)(H_2O)$_2$]·*n*H_2O (1)

To a solution of *D*-H_2muala (27.7 mg, 0.1 mmol) in LiOH (4.8 mg, 0.2 mmol) in H_2O (1 mL), Mg(CH_3COO)$_2$·4H_2O (21.4 mg, 0.1 mmol) in H_2O (1 mL) was added. The yellow clear solution was obtained initially. Upon standing undisturbed at ambient temperature, aggregation of fiber occurred. The resulting fibrous membrane was collected after 2 weeks and air dried.

The solid powder was obtained by slow evaporation from methanolic solution of *D*-H_2muala (27.7 mg, 0.1 mmol) in LiOH (4.8 mg, 0.2 mmol) in MeOH (2 mL) and Mg(CH_3COO)$_2$·4H_2O (21.4 mg, 0.1 mmol) in MeOH (2 mL). The precipitate is washed with MeOH and Et_2O then dried under vacuum. [Mg(*D*-muala)(H_2O)$_2$], Yield: 26 mg (77%). Anal. Calcd. For $MgC_{14}H_{17}NO_7$ (335.6): calcd. C 50.11, H 5.11, N 4.17; found C 51.40, H 5.37, N 4.17. ^{1}H NMR (D_2O, 300 MHz, ppm): δ = 7.46 (d, 1H, Ar), 6.65 (d, 1H, Ar), 5.86 (s, 1H, Ar), 4.17 (d, 2H, -CH_2NH), 3.51 (q, 1H, -CH-Me), 2.31 (s, 3H, -ArCH_3), 1.52 (d, 3H, -CH_3). ESI-MS: 276.1 [*D*-muala]$^-$, 398.1 [Mg(*D*-muala)(H_2O)$_2$(CH_3OH)$_2$]$^-$, 615.1 [Mg_2(*D*-muala)$_2$(H_2O)]$^-$. Weight loss as per TGA: 9.6% (calculated for 2 H_2O: 10.7%).

Synthesis of hydrogel [Mg(*D*-muala)(H_2O)$_2$]·*n*H_2O (2)

To a solution of *D*-H_2muala (27.7 mg, 0.1 mmol) in LiOH (7.2 mg, 0.3 mmol) in H_2O (1 mL), $Mg(CH_3COO)_2\cdot 4H_2O$ (21.4 mg, 0.1 mmol) in H_2O (1 mL) was added. The opaque hydrogel was formed instantly.

The solid powder was obtained by slow evaporation from methanolic solution of *D*-H_2muala (27.7 mg, 0.1 mmol) in LiOH (7.2 mg, 0.3 mmol) in MeOH (2 mL) and $Mg(CH_3COO)_2\cdot 4H_2O$ (21.4 mg, 0.1 mmol) in MeOH (2 mL). The precipitate is washed with MeOH and Et_2O then dried under vacuum. [Mg(*D*-muala)(H_2O)$_2$], Yield: 22 mg (66%). Anal. Calcd. For $MgC_{14}H_{17}NO_7$ (335.6): calcd. C 50.11, H 5.11, N 4.17; found C 49.83, H 5.42, N 3.80. ESI-MS: 276.1 [*D*-muala]$^-$, 398.1 [Mg(*D*-muala)(H_2O)$_2$(CH_3OH)$_2$]$^-$, 615.1 [Mg_2(*D*-muala)$_2$(H_2O)]$^-$. Weight loss as per TGA: 9.9% (calculated for 2 H_2O: 10.7%).

*** Elemental and thermal analysis were performed on dried powder obtained from methanol solution while FTIR and ESI-MS studies were performed on dried sample thread **1** and hydrogel **2**.*

Synthesis of [Mg(*DL*-muala)(H_2O)$_2$] (3)

To a solution of *DL*-H_2muala (27.7 mg, 0.1 mmol) in LiOH (4.8 mg, 0.2 mmol) in LiOH (4.8 mg, 0.2 mmol) in MeOH (2 mL) and $Mg(CH_3COO)_2\cdot 4H_2O$ (21.4 mg, 0.1 mmol) in MeOH (2 mL). The precipitate is washed with MeOH and Et_2O then dried under vacuum. [Mg(*DL*-muala)(H_2O)$_2$], Yield: 23 mg (69%). Anal. Calcd. For $MgC_{14}H_{17}NO_7$ (335.6): calcd. C 50.11, H 5.11, N 4.17; found C 51.27, H 5.68, N 4.21. ESI-MS: 276.2 [*DL*-muala]$^-$, 398.2 [Mg(*DL*-muala)(H_2O)$_2$(CH_3OH)$_2$]$^-$, 615.1 [Mg_2(*DL*-muala)$_2$(H_2O)]$^-$. Weight loss as per TGA: 11.5% (calculated for 2 H_2O: 10.7%).

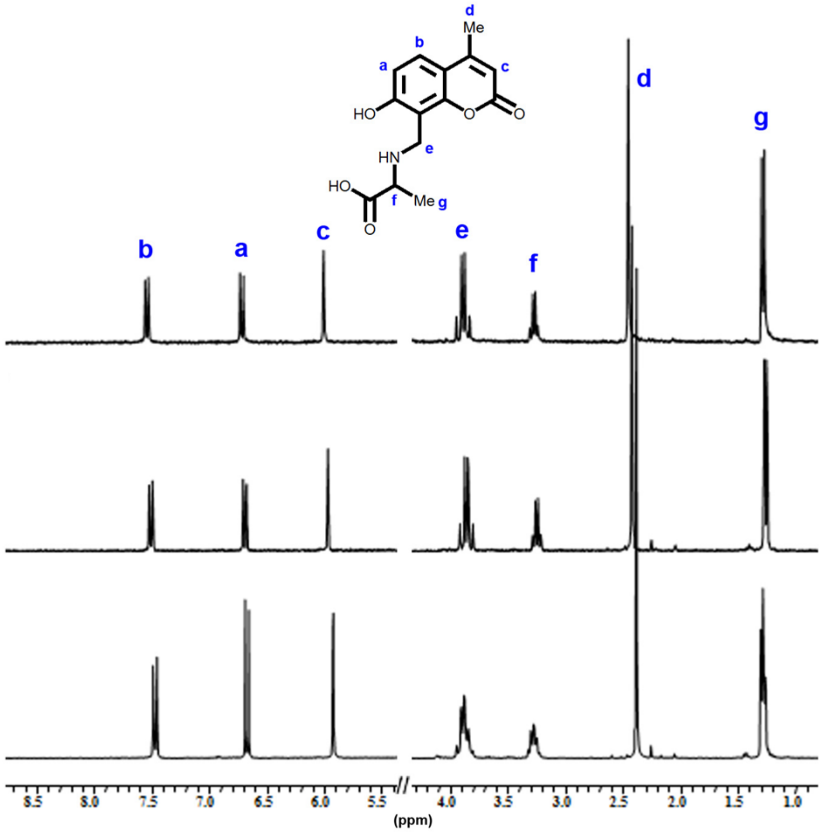


Figure S1. ^{1}H NMR spectra of ligands *L*-H_2muala (top) , *D*-H_2muala (middle) and *DL*-H_2muala (bottom) in D_2O solution.

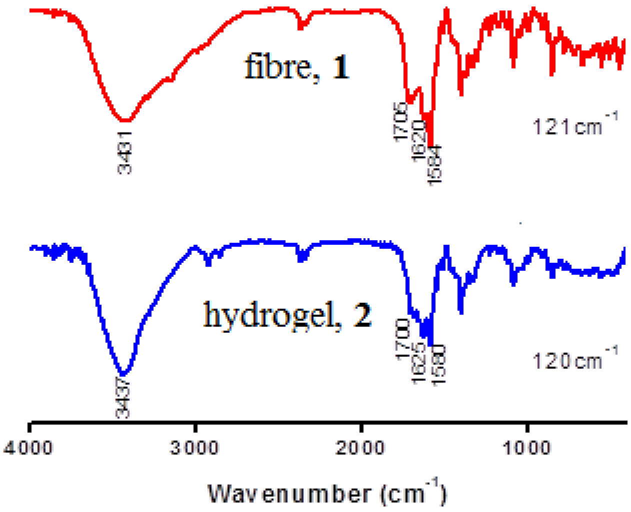


Figure S2. FTIR spectra of **1** and **2**.

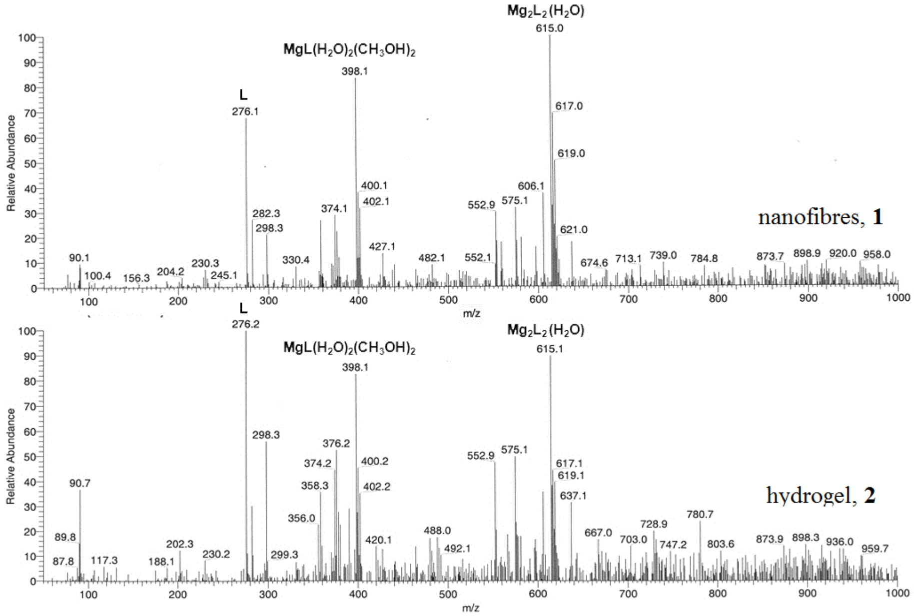


Figure S3. ESI-MS of nanofibre,**1** and hydrogel, **2**.

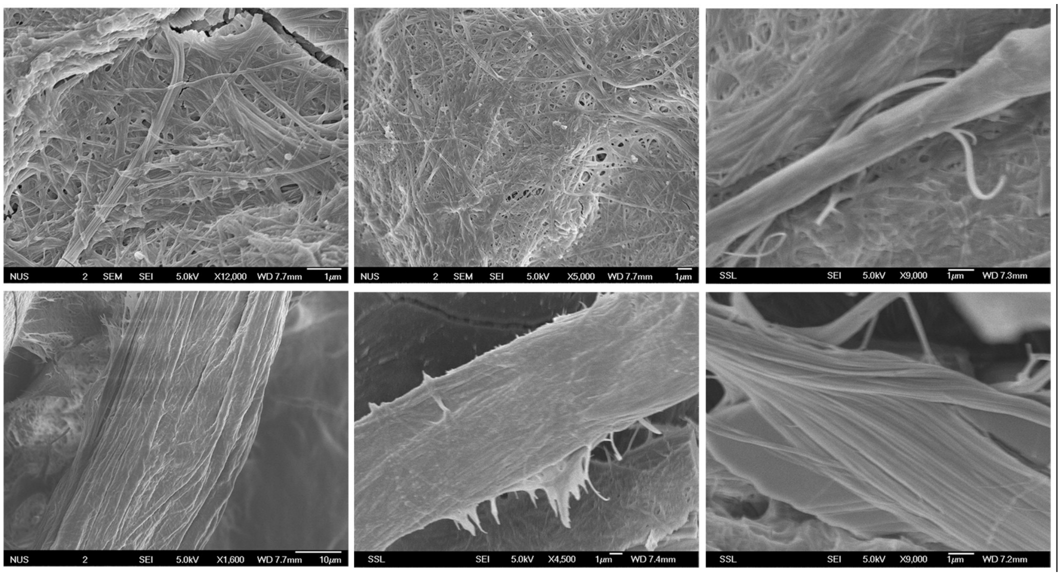


Figure S4. SEM images of nanofibres, **1** at different magnifications showing the fibrous network comprised of aligned nanofibers.

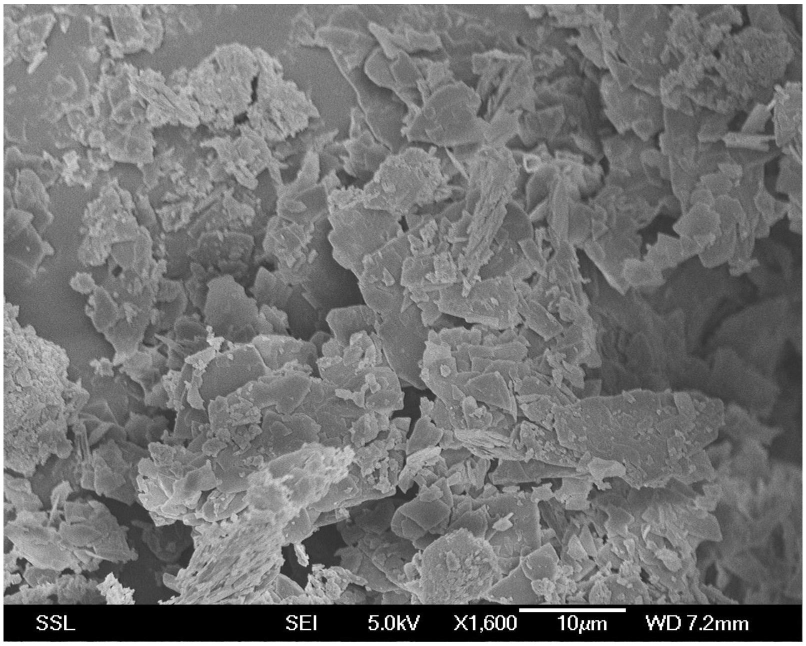


Figure S5. SEM image of compound **3**.

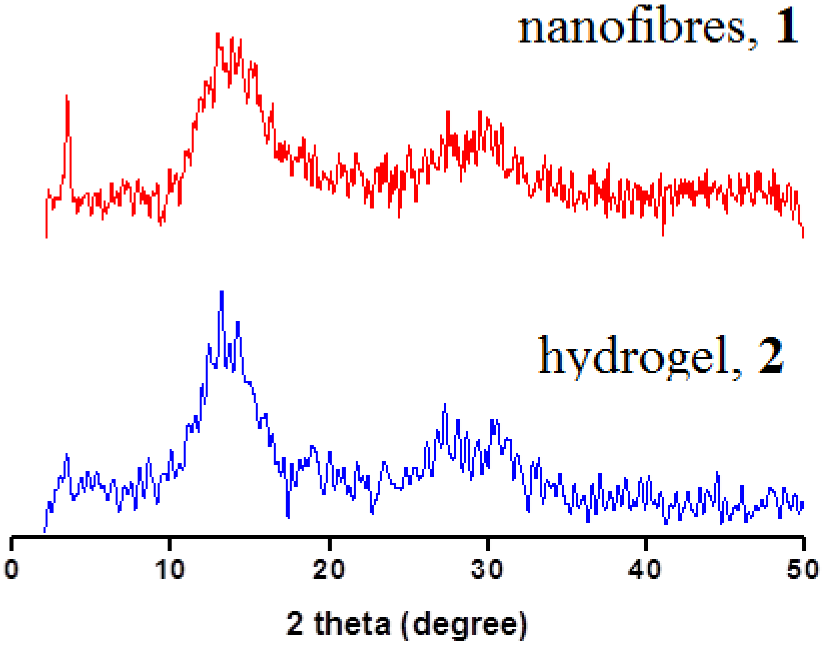


Figure S6. XRPD of nanofibres **1** and hydrogel **2**.

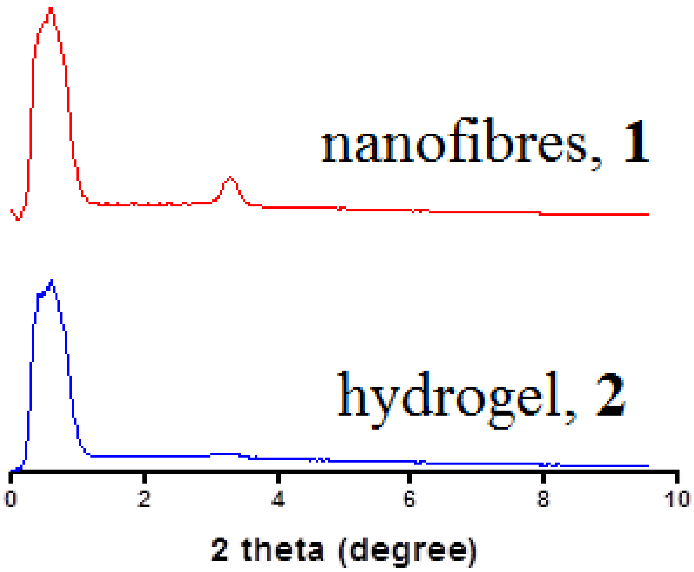


Figure S7. Small angle XRPD of nanofibres **1** and hydrogel **2**.

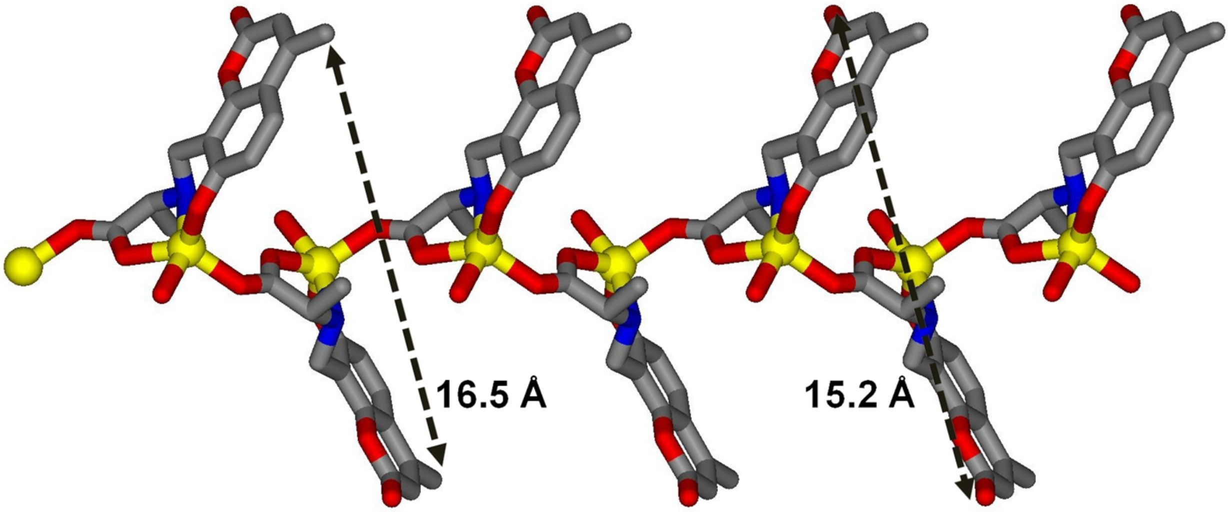
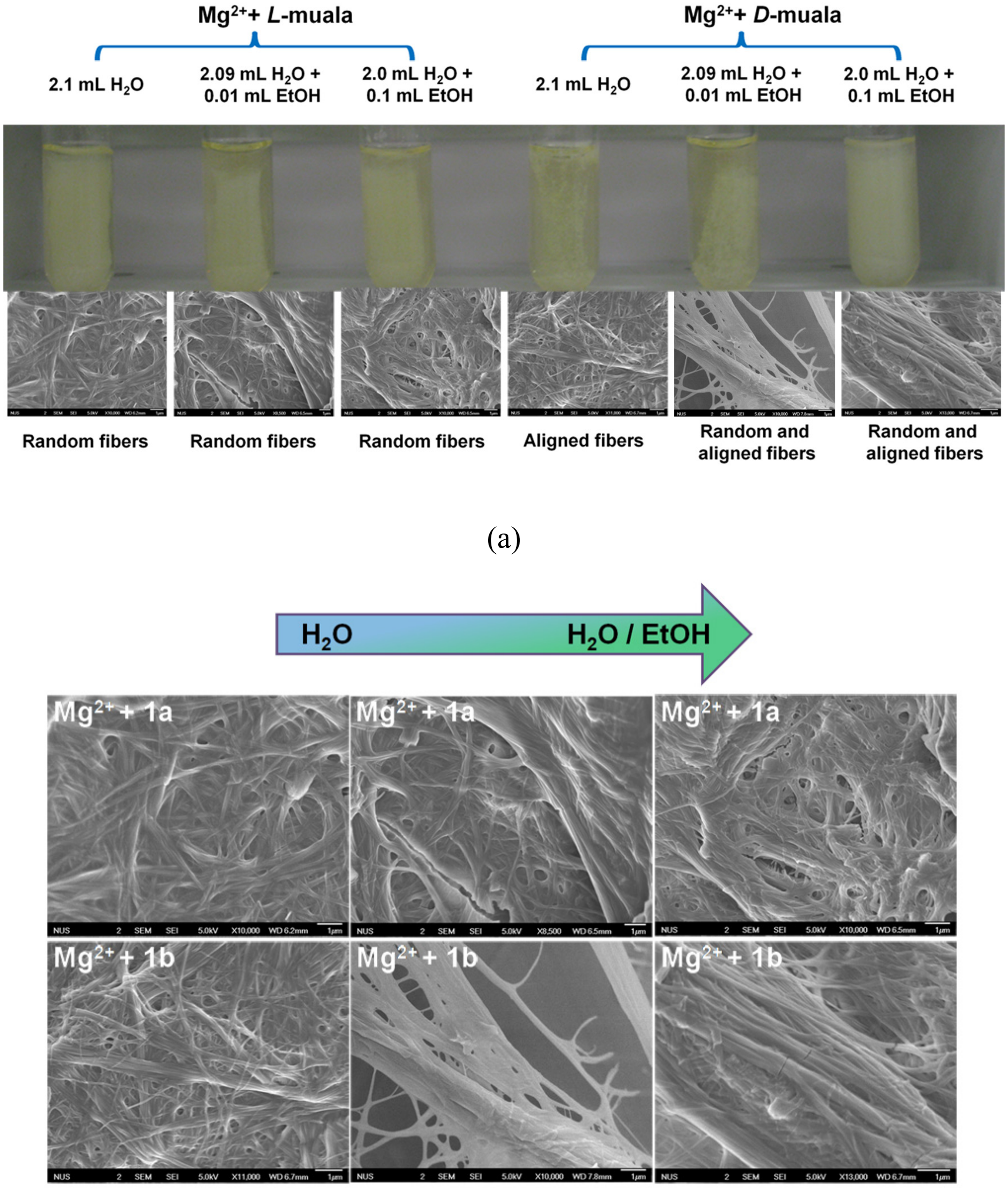


Figure S8. A portion of polymeric chain in [Zn(*L*-muala)(H_2O)]·0.5H_2O.[2]



(a)

(b)

Figure S9. (a) Self-assembly of Mg^{2+} with *L*-H_2-muala (**1a**) and *D*-H_2-muala (**1b**) in different solvent systems. The photograph shows the appearance of reaction mixtures while the SEM images illustrate the microscopic morphology of the products; (b) SEM images of the products obtained from the reaction mixtures from (a).

Microscopic morphology tuning of nanofibers by changing the chirality of ligands and solvents. Reactions of Mg^{2+} with *L*-H_2-muala afforded gelatin-like appearance and random cross-linked network regardless the amount of EtOH while the presence of EtOH in minor amount resulted in the formation of aligned and random nanofibers and gelatin-like appearance in the solution of Mg^{2+} with *D*-H_2-muala.

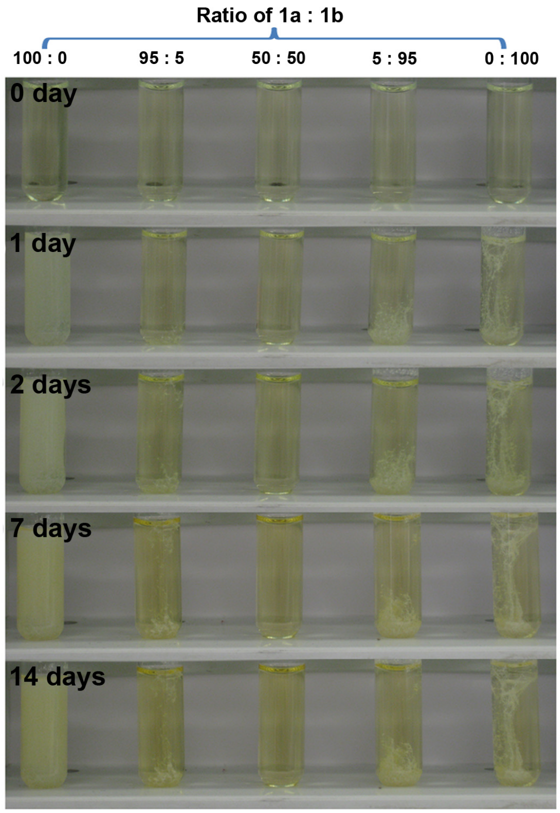
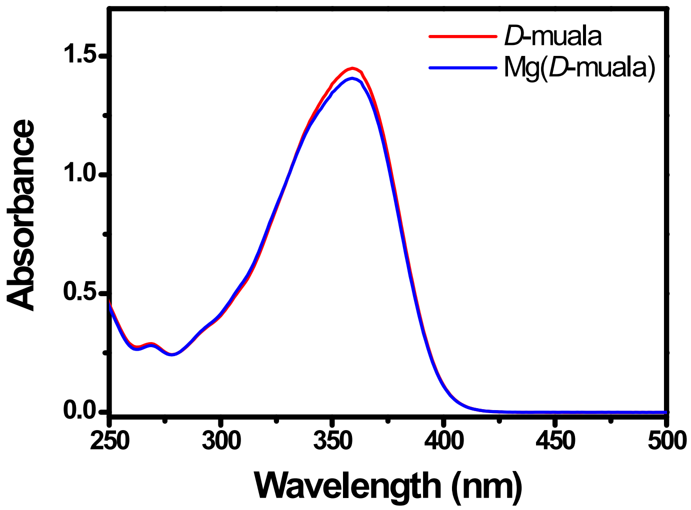
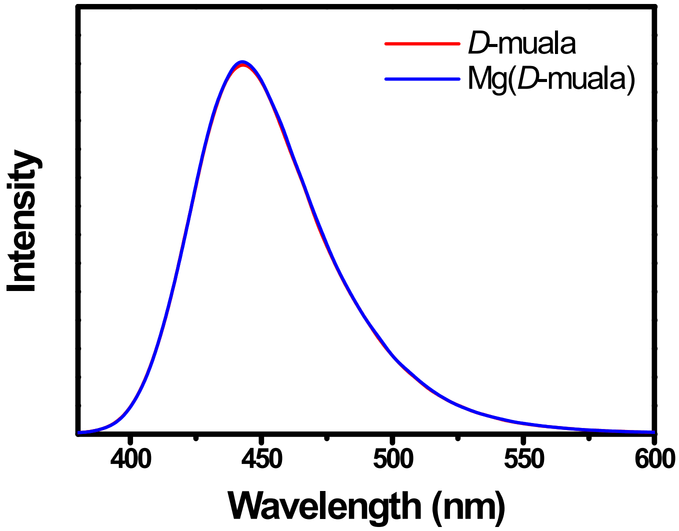


Figure S10. Photograph showing the solution mixture of Mg^{2+} with H_2muala with different chirality at equivalent molar ratio in aquoues solution for 14 days. The molar fractions of ligand *L*- H_2muala and *D*- H_2muala) used were varied from 100:0, 95:5, 50:50, 5:95, 0:100



(a)



(b)

Figure S11. (a) UV-vis absorption and (b) fluorescence spectra of H_2*D*-muala ([H_2*D*-muala] = 1 x 10^{-4} M) in the presence of two equivalent of LiOH and one equivalent of Mg(II) in aqueous solution.

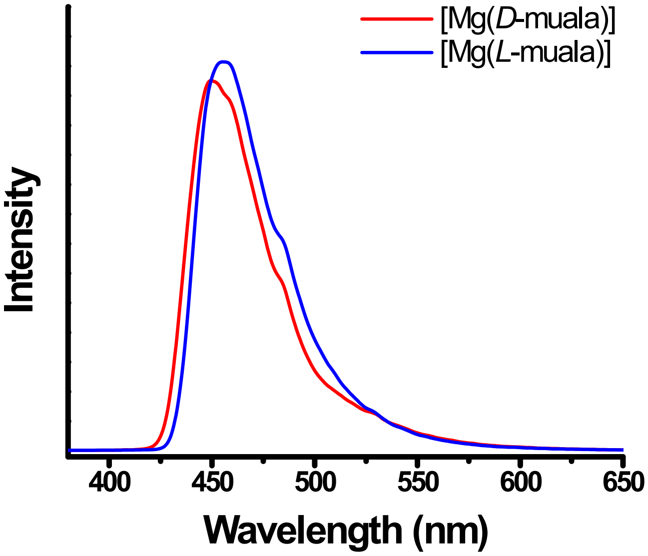


Figure S12. Fluorescence spectra of Mg(II) hydrogels obtained from *L*- and *D*-muala ligands upon excitation at $\lambda = 360$ nm.

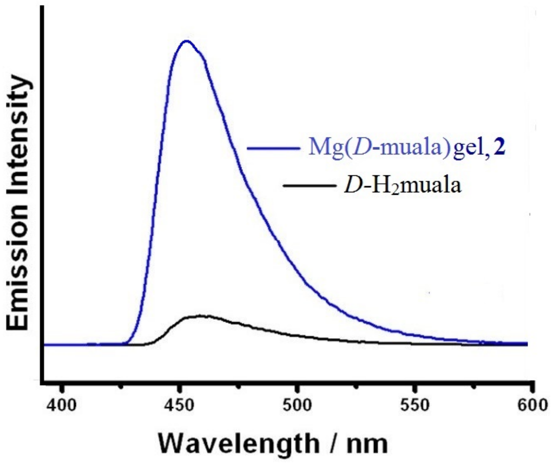


Figure S13. Fluorescence spectra of *D*-H_2muala and Mg(*D*-muala) hydrogel, **2** upon excitation at λ = 360 nm.

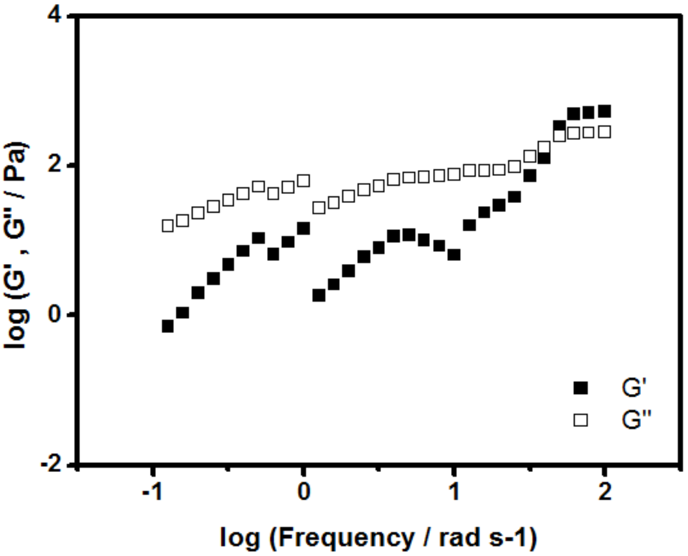


Figure S14. Dynamic frequency sweep measurements of *G'* and *G''* for a solution containing thread **1** at a strain of 2% and 25°C.

Frequency sweep of solution (pH 10, aging for 2 weeks) containing fibre **1** is shown in Fig. 4a. At lower frequencies the loss modulus *G″* is higher than the storage modulus *G′* exhibiting a more viscous than elastic response of the system. A crossover frequency at which *G′* and *G″* become equal was noticed about 50 rad s^{-1}. Exceeding this frequency the former viscous feature transforms into a more elastic one. These findings reflect that the solution of fibre is viscous and entangled network.

References:

1. W. L. Leong, S. K. Batabyal, S. Kasapis and J. J. Vittal, *Chem. Eur. J.*, 2008, **14**, 8822
2. W. L. Leong, A. Y.-Y. Tam, S. K. Batabyal, L. W. Koh, S. Kasapis, V. W.-W. Yam and J. J. Vittal, *Chem. Commun.*, 2008, 3628-3630