Electronic Supplementary Information (ESI)

Crisscrossing coordination networks: ligand doping to control chemomechan-ical properties of stimuli-responsive metallogels

Junghwan Kim and Dongwhan Lee*

Department of Chemistry, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Korea

Experimental Section

General Considerations. All reagents were obtained from commercial suppliers and used as received unless otherwise noted. All air-sensitive manipulations were carried out under argon atmosphere by standard Schlenk-line techniques. The compounds 2^{1} , 5^{2} , and 9^{3} were prepared according to literature procedures.

Physical Measurements. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DPX-300 (300 MHz) or a Varian/Oxford As-500 (500 MHz) spectrophotometer. Chemical shifts in the ¹H NMR spectra were reported in parts per million (ppm) on the δ scale with respect to the internal standard of tetramethylsilane ($\delta = 0.00$ ppm), or peak of residual dimethyl sulfoxide ($\delta = 2.50$ ppm). Data for ¹H NMR spectra were reported as follows: chemical shift, multiplicity (s = singlet, br = broad), coupling constant in Hertz (Hz) and integration. Data for ¹³C NMR spectra were reported as chemical shift in ppm from the peak of residual acetone ($\delta = 29.840$ ppm) or dimethyl sulfoxide $(\delta = 39.520 \text{ ppm})$. High-resolution electrospray ionization (ESI) mass spectra were obtained on an ESI-Q-TOF mass spectrometer (Compact, Bruker Daltonics Inc) at the Organic Chemistry Research Center at Sogang University. FT-IR spectra were recorded on a Shimadzu IR Tracer-100 FT-IR Spectrometer with FelixGX software. Storage and loss moduli were measured on a Discovery Hybrid HR-2 rheometer. HPLC analyses were performed on a Shimadzu Prominence LC-20A equipped with a SPD-20A UV detector and a Shim-pack GIS-ODS column (5 μ m, size = 250 × 4.6 mm). Powder X-ray diffraction patterns (PXRD) were collected using a Rigaku SmartLab diffractometer operated at 3 kW with monochromatic Cu-K $\alpha 1$ ($\lambda = 1.5406$ Å) radiation and with the scan range of $2\theta = 5-90^{\circ}$. FESEM studies were carried out on a JSM-7800F Prime (JEOL), operating at 1–10 kV. To minimize sample charging, samples were coated with a thin layer of Pt before measurements. EDX mapping was carried out with SDD type 80 mm² EDS X-MAS detector (Horiba), coupled with FESEM (Hitachi, SU-8020). TEM studies were carried out on a JEM1010 electron microscope (JEOL), operating at 120 kV. For TEM measurements, aerogel particles were embedded in epoxy resin, and hardened at 70 °C for 12 h. A HM 340E microtome (Microm Lab) was used to prepare ultrathin sections of ca 80 nm thickness from the resin-embedded aerogels.

4,4'-Dihydroxy-[1,1'-biphenyl]-3,3',5,5'-tetracarbaldehyde tetraoxime (1). A 250-mL roundbottom flask was charged with 5 (1.82 g, 6.12 mmol), NH₂OH-HCl (8.51 g, 123 mmol), EtOH (100 mL), and a magnetic stir bar. The reaction mixture was stirred for 10 min at r.t., treated with KOAc (11.63 g, 118.7 mmol), and heated at reflux for 3 h. After cooling to r.t., the reaction mixture was concentrated under reduced pressure, and treated with water (500 mL) to induce precipitation. The resulting solid material was isolated by filtration, washed with water (200 mL), and acetone (500 mL), and dried in air to afford 1 as a pale yellow powder (1.64 g, yield = 75%). ¹H NMR (300 MHz, DMSO- d_6 , 298 K): δ 11.60 (br s, 4H), 10.88 (br s, 2H), 8.45 (s, 4H), 7.83 (s, 4H). ¹³C NMR (75 MHz, DMSO- d_6 , 298 K): δ 154.22, 147.37, 131.07, 126.66, 120.09. FT-IR (ATR, cm⁻¹): 3383, 3207, 3151, 3116, 3030, 2983, 2958, 1980, 1859, 1755, 1651, 1622, 1593, 1485, 1454, 1409, 1406, 1336, 1308, 1271, 1022, 993, 951, 866, 802, 758. HRMS (ESI) calcd for C₁₆H₁₅N₄O₆ [M + H]⁺ 359.0986, found 359.0988.

3,3',5,5'-Tetrakis((methylimino)methyl)-[1,1'-biphenyl]-4,4'-diol (6). A 15-mL thick-walled reaction tube was charged with **5** (100 mg, 0.337 mmol), MeOH (4 mL), and a magnetic stir bar. With stirring, methylamine (40% in water; 0.2 mL, 2 mmol) was delivered using a syringe. The reaction vessel was sealed tightly, heated at 100 °C for 17 h, and cooled to r.t. Volatile fractions were removed under reduced pressure to afford **6** as a shimmering red solid (72 mg, yield = 61%). ¹H NMR (300 MHz, DMSO- d_6 , 298 K): δ 8.73 (s, 4H), 7.98 (s, 4H), 3.48 (s, 12H). ¹³C NMR (75 MHz, DMSO- d_6 , 298 K): δ 163.21, 162.78, 129.57, 128.22, 122.11, 46.16. FT-IR (ATR, cm⁻¹): 3357, 2884, 2772, 2115, 1981, 1636, 1600, 1526, 1442, 1401, 1362, 1288, 1254, 1199, 1138, 1080, 1011, 958, 866, 798, 759, 668. HRMS (ESI) calcd for C₂₀H₂₃N₄O₂ [M + H]⁺ 351.1816, found 351.1814.

4,4'-Dimethoxy-[1,1'-biphenyl]-3,3',5,5'-tetracarbaldehyde (7). A 20-mL vial was charged with 5 (101 mg, 0.339 mmol), K₂CO₃ (0.512 g, 3.70 mmol) and DMF (10 mL). The mixture was stirred for 5 min, and CH₃I (0.22 mL, 3.5 mmol) was added in a single portion. The reaction was heated at 90 °C for 12 h, cooled to r.t., and mixed with CH₂Cl₂ (150 mL). The organic layer was washed with water (3 × 150 mL), sat'd aq NH₄Cl (150 mL), and brine (150 mL). The organic fraction was dried over anhyd MgSO₄ and filtered. Volatile fractions were removed under reduced pressure to furnish 7 as an off-white solid (31 mg, yield = 27%). ¹H NMR (300 MHz, acetone- d_6 , 298 K): δ 10.37 (s, 4H), 8.40 (s, 4H), 4.09 (s, 6H). ¹³C NMR (75 MHz, CDCl₃, 298 K): δ 206.99, 189.75, 133.41, 130.87, 66.60, 31.16. FT-IR (ATR, cm⁻¹): 3066, 2919, 2875, 2850, 2755, 2151, 1982, 1744, 1681, 1600, 1568, 1456, 1415, 1388, 1328, 1295, 1243, 1224, 1181, 1085, 984, 958, 895, 830, 843, 830, 817, 793, 760, 719, 650, 604. Anal. Calcd for C₁₈H₁₄O₆·0.5H₂O: C, 64.48; H, 4.51. Found: C, 64.87; H, 4.73.

4,4'-Dimethoxy-[1,1'-biphenyl]-3,3',5,5'-tetracarbaldehyde tetraoxime (8). A 15-mL thickwalled reaction tube was charged with 7 (113 mg, 0.347 mmol), MeOH (5 mL), and a magnetic stir bar. With stirring, NH₂OH-HCl (252 mg, 3.63 mmol) and KOAc (304 mg, 3.10 mmol) were added successively. The reaction vessel was sealed, and heated at 90 °C for 6 h. After cooling to r.t., the mixture was poured into water (50 mL) to induce precipitation. The resulting solid material was isolated by filtration, and washed with water (50 mL). The residual material was taken up in acetone (50 mL), dried over anhyd MgSO₄, and filtered. Volatile fractions were removed under reduced pressure to afford 8 as an off-white solid (87 mg, yield = 65%). ¹H NMR (300 MHz, acetone- d_6 , 298 K): δ 10.66 (s, 4H), 8.41 (s, 4H), 8.10 (s, 4H), 3.89 (s, 6H). ¹³C NMR (75 MHz, acetone- d_6 , 298 K): δ 156.43, 143.41, 135.91, 127.54, 125.06, 63.32. FT-IR (ATR, cm⁻¹): 3235, 3004, 2925, 2051, 1982, 1700, 1622, 1455, 1412, 1314, 1259, 1212, 1175, 1082, 996, 952, 881, 850, 709, 679, 611. HRMS (ESI) calcd for C₁₈H₁₈N₄O₆Na [M + Na]⁺ 409.1119, found 409.1117. Synthesis of Metallogels. A solution of the ligand $(50 \text{ mg})^4$ in DMF (1.0 mL) was treated with Et₃N (0.12 mL, 0.84 mmol). With stirring, a DMF solution (3.0 mL) of Zn(acac)₂·xH₂O (140 mg, 0.42 mmol) was added rapidly. A yellow gel-like material formed instantaneously. The reaction mixture was sonicated for 5 min, and heated at 90 °C for 4 h for thermal annealing. Formation of a stable gel was confirmed by an inversion test of the container to show no flow of the material inside. This synthetic protocol is applicable to other transition metals including copper(II) and cobalt(II) to prepare metallogels with weight percentages ranging 2–10 wt%.

Preparation of Aerogels. A sample chamber built for supercritical drying was charged with metallogel (< 10 mL). The chamber was sealed, and placed in a high pressure reactor. After assembling the reactor, supercritical CO₂ (200 mL; 200 bar; T = 45 °C) was allowed to flow (0.3 mL/min) to remove the solvent and unreacted soluble components from the metallogel matrix.

Rheological Measurements. Mechanical properties of the metallogels were determined by using a rheometer (Discovery Hybrid HR-2 rheometer, TA Instruments, USA). Frequency sweeps were performed in the angular frequency range of 0.1 to 100 rad/s at strain (1%) in the linear region to determine the storage (G') and loss (G'') moduli.

Gelation-Degelation Studies. A DMF stock solution of 1 (0.14 M) and Et₃N (0.84 M; 6 equiv) was prepared (Solution A). A DMF stock solution of 2 (0.28 M) and Et₃N (0.84 M; 3 equiv) was also prepared (Solution B). For gelation studies, Solution A and Solution B were delivered in varying volume ratios to a custom-built glass tube, while keeping the final volume fixed to 0.3 mL, so that an identical "amount" of ligand donors (from 1 and 2 combined) are present in each of the 11 reaction batches prepared separately. To each reaction vessel, one drop of methyl orange stock solution (0.10 M in DMF) was added. A DMF stock solution (0.9 mL) of $Zn(acac)_2 \cdot xH_2O$ (0.14 M) was delivered in a single portion using a syringe, and the resulting yellow gel was kept at r.t. for 10 min. For acid-triggered degelation studies, a portion of neat TFA (2.0 mL) was layered on top of the gel. The progress of the reaction was recorded by taking digital images at fixed time intervals.

Degelation Studies under Gas Flow Conditions. A custom-built Teflon sample holder was loaded with metallogel (0.4 mL), and positioned inside a glass cylinder. The cylinder was connected to inlet and outlet for the HCl/N_2 gas stream (see Figures 6 and S6 for details), and tilted by 10° to facilitate drainage of the de-gelated material. The assembled unit was subjected to a constant flow (0.5 L/min) of gaseous HCl (5%, v/v). The progress of acid-triggered degelation reaction was monitored by taking digital images at fixed time intervals.

Acid Digestion and Ligand Analysis. Aerogel sample (ca 100 mg) was placed inside a 4-mL vial, treated with conc HCl (2 mL), and sonicated for 30 min. The resulting precipitate was isolated by filtration through a fritted glass filter, washed with conc HCl (2 mL) and water (2 mL), and dried in air. The isolated solid material was extracted into DMSO- d_6 for ¹H NMR analysis, and subsequent HPLC measurement.



Fig. S1. (a) A schematic diagram of the experimental setup for supercritical CO₂ (SCO2) drying. (b) Photographic images of the aerogel samples of 1 and transition metal ions (Co(II), Cu(II), and Zn(II); from left to right, respectively) prepared by SCO2 drying (0.3 mL/min; 200 mL; 200 bar; T = 45 °C).



Fig. S2. SEM image of the Zn metallogel (top left) and energy dispersive X-ray (EDX) elemental mapping of carbon, oxygen, nitrogen, and zinc.



Fig. S3. SEM image of the Co metallogel (top left) and energy dispersive X-ray (EDX) elemental mapping of carbon, oxygen, nitrogen, and cobalt.



Fig. S4. SEM image of the Cu metallogel (top left) and energy dispersive X-ray (EDX) elemental mapping of carbon, oxygen, nitrogen, and copper.



Fig. S5. IR spectrum of (a) free ligand 1, and (b) aerogel prepared by SCO2 drying of Zn metallogel.



Fig. S6. (a) A schematic diagram of custom-built gas-line for controlled delivery of N_2 and HCl gas mixture, and (b) photographic image of the actual experimental setup.



Fig. S7. Digital images taken at fixed time intervals (see *y*-axis) after exposure of metallogel samples of (a) cobalt(II), (b) copper(II), and (c) zinc(II) prepared with the ligand 1 at varying wt% (see *x*-axis).



Fig. S8. Storage and loss modulus of F1–F10 determined at $\omega = 10$ rad/s. For the sample F8, contraction of the gel volume and release of the entrapped solvent was observed.



Fig. S9. (a) IR spectra of the free ligand 1 (red) and 2 (blue). (b) Overlaid IR spectra of aerogel samples of formulations F1-F7.



OH.

Fig. S10. Partial ¹H NMR spectra of acid hydrolysis reaction products of the mixed-ligand aerogels (a) **B** (with 1:2 = 75:25, wt/wt%), (b) **C** (with 1:2 = 50:50, wt/wt%), and (c) **D** (with 1:2 = 25:75, wt/wt%). For each formulation, the bulk sample was divided into three batches, which were individually subjected to acid hydrolysis and isolation/extraction prior to analysis. Shown in (d) is a plot of mol% of ligand **2** used in synthesis (*x*-axis) vs isolated in the acid-digested prouducts (*y*-axis). See the chemical structures shown on the right side for the assignment of the proton resonances used in peak integration.



Fig. S11. (a) A representative HPLC chromatogram of the acid hydrolysis product of mixed-ligand metallogel (prepared initially with 1:2 = 50:50, wt/wt%, and dried with scCO₂), compared with those of (b) ligand 2, and (c) ligand 1. Shown in (d) is a plot of mol% of ligand 2 used in synthesis (*x*-axis) vs its relative peak area in the HPLC chromatograms of acid hydrolysis products (*y*-axis).



Fig. S12. Powder X-ray diffraction patterns of mixed-ligand aerogel samples (a) A (with 1:2 = 100:0, wt/wt%), (b) B (with 1:2 = 75:25, wt/wt%), (c) C (with 1:2 = 50:50, wt/wt%), and (d) D (with 1:2 = 25:75, wt/wt%), compared with those of (e) free ligand 2, (f) free ligand 1, and (g) Zn(acac)·xH₂O.



batch A1

batch A2

batch A3



batch B1

batch D1

batch **B2**

batch B3

batch D3



Fig. S13. SEM images and energy dispersive X-ray (EDX) elemental mapping (carbon, oxygen, nitrogen, and zinc) of metallogel samples (a) A (with 1:2 = 100:0, wt/wt%), (b) B (with 1:2 = 75:25, wt/wt%), (c) C (with 1:2 = 50:50, wt/wt%), and (d) D (with 1:2 = 25:75, wt/wt%). For each formulation, the bulk sample was divided into three batches for individual measurements, resulting in a total of 12 data sets shown here.

batch D2



Fig. S14. Plots of acid-triggered de-gelation time of Zn metallogels (4 wt%) prepared in different ligand-to-metal ratios.



Fig. S15. ¹H NMR (300 MHz) spectrum of 1 in DMSO- d_6 (T = 298 K).



Fig. S16. ¹³C NMR (75 MHz) spectrum of 1 in DMSO- d_6 (T = 298 K).







Fig. S17. High-resolution mass spectrum of 1.



Fig. S18. ¹H NMR (300 MHz) spectrum of 6 in DMSO- d_6 (T = 298 K).



Fig. S19. ¹³C NMR (75 MHz) spectrum of 6 in DMSO- d_6 (T = 298 K).







Fig. S20. High-resolution mass spectrum of 6.



Fig. S21. ¹H NMR (300 MHz) spectrum of 7 in acetone- d_6 (T = 298 K).



Fig. S22. ¹³C NMR (75 MHz) spectrum of 7 in acetone- d_6 (T = 298 K).



Fig. S23. ¹H NMR (300 MHz) spectrum of 8 in DMSO- d_6 (T = 298 K).



Fig. S24. ¹³C NMR (75 MHz) spectrum of 8 in DMSO- d_6 (T = 298 K).







Fig. S25. High-resolution mass spectrum of 8.

References

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(4) Corresponding to 0.14 mmol of 1, and producing metallogels of 4 wt%.