Supporting Information

Self-healing and moldable material with deformation recovery ability from self-assembled supramolecular metallogels

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1. General remarks

¹H NMR spectra were obtained with a Bruker AV-400 (400 MHz) or Varian INOVA-400 (400 MHz), while ¹³C NMR spectra were recorded on a Bruker AV-400 (100 MHz) or arian INOVA-400 (100 MHz). The ¹H and ¹³C NMR chemical shifts were measured relative to (CD₃)₂SO as the internal references. Mass spectra were obtained by a Finnigan-LCQ^{DECA} instrument. Elemental analyses were performed with a CARLO ERBA1106 instrument. Transmission electron microscopy (TEM) studies were carried out on a HITACHI H-600, operating at 100 kV. Tapping mode AFM imaging was performed under ambient conditions on a SEIKO SPA400 instrument by using BS-Tap 300Al levers (Budget Sensors, silicone cantilevers). Dynamic light scattering (DLS) experiment was performed with a Brookhaven BI-200SM instrument at 25 °C. Rheological characterisation was performed on a HAAKE MARS III produced by Thermo Scientific Instruments. A parallel plates viscometer (diameter: r = 35 mm) was used with a cap to prevent the evaporation of the solvent and the gap between the plates is 1 mm. Data was collected and analysed using the HAAKE RheoWin 3 software produced by Thermo Scientific Instruments. Data presented here is for gel 1 at 4 % by weight. Frequency sweep measurement was performed at 25 °C and the stress amplitude was maintained at 100 Pa and 17 data points were taken between 0.0215 and 10 Hz. Stress amplitude oscillations were taken after the frequency oscillations experiments. The temperature was held at 25 °C. A frequency of 1 Hz was used and 40 data points were taken over the entire stress amplitude range.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Unless otherwise indicated, all syntheses and manipulations were carried out under dry N_2 atmosphere. Anhydrous solvents were dried by standard procedures.

Preparation of samples for AFM. Samples of the solution of gel **1-4** (0.01 wt%) in DMF were cast onto a freshly cleaved mica under ambient conditions, and then dried at 55 \degree for 0.5 h before making AFM images.

Preparation of samples for TEM. TEM specimens were prepared by gently placing a carbon-coated copper grid on a surface of the sample. The TEM grid was removed, dried for 0.5 h at room temperature, and then subjected to observation.

Gelation tests. A capped vial was charged with a N,N-dimethylformamide (DMF) solution of **1-4** (1.5 wt%) and a DMF solution of Pd(OAc)₂ (1.5 wt%), and the mixture was then placed for several seconds or minutes. The sample was prepared and simply confirmed by the "stable to inversion of a test tube" method.

2. Procedures for the preparation of 5-substituted *1H*-tetrazole ligands 1-4^[S1, S2] and methyl derivative 5^[S3]

General Procedure for the Transformation of Nitriles into Tetrazoles.

In a typical experiment, a mixture of the nitrile (40 mmol), sodium azide (3.00 g, 60 mmol) and ammonium chloride (2.96 g, 52 mmol) in dry DMF (100 mL) was heated under 120 °C until TLC showed complete conversion (*ca.* 14h). Then 4 N HCl was added and the resulted crude product was collected by filtration (for 5-methyltetrazole and 5-dodecyl-1H-tetrazole, ethyl ester was used for extraction).

1, 3-Bis (5-tetrazolyl)benzene (1): Recrystallization from the mixture of DMF and MeOH yielded the product (94 %). m.p. >300 °C, ¹H NMR (400 MHz, DMSO- d^6): δ 7.86 (t, J = 6.8 Hz, 1H), 8.24 (d, J = 7.2 Hz, 2H), 8.80 (s, 1H) ppm; MS calcd for [M+1] ⁺: 215.1; found: 215.3; Anal. calcd for C₈H₆N₈: C, 44.86; H, 2.82; N, 52.32; found: C, 44.79; H, 2.90; N, 52.35.

5-methyltetrazole (2): The reaction mixture was stirred in a pressure tube submerged in an oil bath at 120 °C and the product **2** was obtained in 56 % yield. m.p.:147 °C; ¹ H NMR (400 MHz, DMSO- d^6): δ 2.50 (s, 3H) ppm; MS calcd for [M+1] ⁺: 85.0; found: 85.4; Anal. calcd for C₂H₄N₄: C, 28.57; H, 4.79; N, 66.64. Found: C, 28.51; H, 4.83; N, 62.58.

5-dodecyltetrazole (**3**): Recrystallization from petroleum ether yielded the product (84%) as a white solid, m.p.: 65-67 °C; ¹ H NMR (400 MHz, CDCl₃): δ 0.78 (t, *J* =7.2, 6.0 Hz, 3H), 1.17-1.34 (m, 18H),1.78-1.82 (m,2H), 3.00-3.03 (m, 2H) ppm; MS calcd for [M+1] ⁺: 239.2; found: 239.6; Anal. calcd for C₁₃H₂₆N₄: C, 65.50; H, 10.99;

N, 23.50; Found: 65.45; H, 11.03; N, 23.36.

5-phenyltetrazole (**4**): Recrystallization from the mixture of DMF and MeOH yielded the product (93 %). m.p.: 215-216 °C; ¹H NMR (400 MHz, DMSO- d^6): δ 7.60-7.61 (m, 3H), 8.04-8.05 (m, 2H) ppm; MS calcd for [M+1] ⁺: 147.1; found: 147.3; Anal. calcd for C₇H₆N₄: C, 57.53; H, 4.14; N, 38.34; Found: C, 57.45; H, 4.20; N, 38.36.

1, 3-bis(1-methyl-5-tetrazolyl)benzene (**5**): To a solution of **1** (0.5 g, 2.33 mmol) in dry DMF (10 ml) at 0 °C was added NaH (0.28 g, 60%, 6.99 mmol). The mixture was stirred at room temperature for 30 min, then CH₃I (0.99 g, 6.99 mmol) was added. After a total stirring of 4 h at 38 °C, the solvent was evaporated and the residue was diluted with CH₂Cl₂. The organic layer was washed with H₂O, and dried over anhydrous Na₂SO₄. The solvent was evaporated and the residue was purified by recrystallization from EtOAc to afford **5** as a white solid (0.51 g, 92%). m.p. >300 °C, ¹H NMR (400 MHz, CDCl₃): δ 4. 42 (s, 6H), 7.69 (t, *J* = 7.6, 8.0 Hz, 2H), 8.35 (d, *J* = 7.6 Hz, 1H), 8.91 (s, 1H) ppm; MS calcd for [M+1] ⁺: 243.1; found: 243.4; Anal. calcd for C₁₀H₁₀N₈: C, 49.58; H, 4.16; N, 46.26; found: C, 49.51; H, 4.23; N, 46.19.

Reference

S1. Z. P. Demko, K. B. Sharpless, J. Org. Chem. 2001, 66, 7945-7950;

S2. S. Fürmeie, J. O. Metzger, Eur. J. Org. Chem. 2003, 885-893.

S3. R. H. Durland, T. S. Rao, V. Bodepudi, D. M. Seth, K. Jayaraman, G. R. Revankar, *Nucleic Acids Research*. **1995**, *23*, 647-653.



3. The DMF-mediated possible coordination mode between the ligand 1 and Pd²⁺.

Figure S1. A schematic representation of the DMF-mediated self-assembly of ligand 1 with Pd^{2+} .

Color code: C (gray), N (purple), O (red) Pd (yellow) and H of ligand 1 (white), H atoms of DMF

and OAc⁻ anion were omitted for clarity.



4. AFM, TEM and DLS images of gel 1, gel 2 and gel 4

Figure S2. (a) Tapping-mode AFM height image of gel **1** in DMF (0.01 %) on a freshly cleaved mica surface after the solvent was evaporated (scale bar: 200 nm), (b) TEM images (unstained) of gel **1** (scale bar: 100 nm) in DMF (0.01 %), (c) The intensity-weighted distribution of the aggregates obtained from the DLS measurement of the sample of gel **1** (0.01 %) in DMF at 25 °C, (d, f) Tapping-mode AFM height images of gel **2** (0.02 %) and gel **4** in DMF (0.01 %) on a freshly cleaved mica surface after the solvent was evaporated, (e, g) the corresponding phase images.

5. Rheological data of gel 1 and the solvent-healed gel



Figure S3. (a) Frequency sweep rheometry of gel **1** (4 %). The angular frequency (Hz), storage modulus G' (Pa) and loss modulus G" (Pa) are shown as log scale. The frequency sweep data showing no crossover point throughout the experimental region, (b, c) Stress sweep rheometry of gel **1** showing G' and G" as functions of stress amplitudes (1000 Pa and 3000 Pa, respectively) at constant frequency 1Hz. Stress amplitude are shown as log scale, (d) The stress sweep rheometry of DMF-healed gel **1** showing the viscoelastic moduli were remained *ca*. 30% of the original values after aging for several days.



6. Swelling behavior of gel 1

Figure S4. (a, b) The swelling behavior of the molded block of gel **1** (original size, 9 mm (length) *8 mm (width), expanded to 12 mm * 10 mm after immersing into DMF for several minutes (less obvious for height)), (c) the gel **1** (4 %, 0.5 mL DMF) could be approximately evolved to double volume gel by absorbing 0.5 mL DMF.

7. The healing process of a thorough cross of gel 1 and water-healed process of gel pieces with methyl red



Figure S5. (a, b) the damaged cross was healed after permeating of H_2O , (c, d) the aqueous solution of methyl red (0.1 %) could not be permeated into the damaged cross. (e, f) the gel **1** with methyl red was broke into pieces and also could be repaired upon adding of H_2O , g) the gel colour was changed after two weeks probably due to the disintegration of methyl red, and the volume was slightly shrank likely because of the volatilization of solvent from less compact network structure in the open vessel.

8. Light transmittance and viscous behavior of gel 1



Figure S6. (a) The clear words could be viewed from the gel **1** (top and bottom, respectively), (b) the block of gel **1** adhered to the surface of a razor.

9. Copies of ¹H spectra of ligands 1-5



Figure S7. ¹H NMR spectra of ligand **1** in DMSO- d_6 at 293K



Figure S8. ¹H NMR spectra of ligand **2** in DMSO- d_6 at 293K



Figure S9. ¹H NMR spectra of ligand **3** in CDCl₃ at 293K



Figure S10. 1 H NMR spectra of ligand **5** in CDCl₃ at 293K