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Coordination polymer gel derived from a tetrazole ligand and Zn^{2+} : spectroscopic and mechanical properties of an amorphous coordination polymer gel[†]

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A tetrazole-based ligand forms a supramolecular gel in the presence of transition metal ions, particularly Zn^{2+} , Cu^{2+} and Co^{2+} . The gels have been characterized by SEM, TEM, fluorescence spectroscopy, rheometry and fluorescence microscopy. The polymer exhibits a strong fluorescence enhancement upon gel formation. According to DFT calculations, one of Zn^{2+} is bound to 4 tetrazole moieties and 2 solvent molecules by octahedral structure. The Zn^{2+} -induced gelation does not strongly depend on anions. The Zn^{2+} -tetrazole ligand gel shows a spherical structure with 20–50 nm diameter. The rheological properties of the Zn^{2+} -tetrazole ligand gel were strongly dependent on the concentration of Zn^{2+} .

Introduction

Organogels and hydrogels composed from small molecules or 'low molecular weight gelators' (LMWGs), which are linker into fibers by supramolecular interactions is a current topic of great interest. Supramolecular gels have been studied as soft materials for use in applications such as drug-delivery systems, tissue engineering, sensing devices, separation and optoelectronic devices.¹⁻¹⁷ The incorporation of labile metals or anions within these supramolecular gels is of particular interest because metallogels and coordination polymer gels with metal-organic framework structures are applicable in various fields such as redox responsiveness,^{18,19} catalytic action,^{20,21} absorption,^{22,23} emission,²⁴⁻²⁷ magnetism²³ and electron emission.²¹ In addition, the gels composed of a metal-organic framework (MOF) structure can be rapidly, efficiently, and easily prepared under mild conditions in comparison to a typical crystalline MOF, which would display similar properties.28

Although there are many reports on the formation of coordination polymer gels, there is relatively little information in the literature regarding the photoluminescence and rheological properties of coordination polymer gels at different concentrations of metal ions.^{24–27} In particular, the rheology of coordination polymer gels might be dependent on the concentration of metal ions and is significantly influenced by the formation process of the coordination polymer structure. Thus, the study for coordination polymer gels in the presence of various concentrations of metal ions is important to our understanding of the formation process of gelation and the resulting physical properties.

With this in mind, we chose tetrazole-appended benzene as the framework for the attachment of ligands because of its well-defined and extensively developed MOF chemistry.²⁹ A tetrazole derivative, with multiple binding sites, promotes cross-linking to form a polymer network that is a critical condition for gelation. Herein, we report the formation of a coordination polymer gel of the tetrazole-based ligand (1) containing Zn^{2+} ion and its influence on the rheological properties of the coordination polymer gels at different concentrations of Zn^{2+} . We also prepared ligand (2), which contains two tetrazole moieties as a reference. Interestingly, its fluorescence intensity is enhanced upon the formation of a coordination polymer gel 1 with Zn^{2+} , relative to sol 1 in organic solvents. The rheology of Zn^{2+} coordination polymer gel 1 strongly depends on the concentration of Zn^{2+} .

Experimental

General

All reagents were purchased from Aldrich and Tokyo Kasei Chemicals and used without further purification.

Characterization

¹H and ¹³C NMR spectra were measured on a Bruker ARX 300 apparatus. IR spectra were obtained for KBr pellets, in the range 400–4000cm⁻¹, with a Shimadzu FT-IR 8400S instrument, and mass spectra were obtained by a JEOL JMS-700 mass

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Downloaded by North Carolina State University on 14 November 2012 "ublished on 01 February 2012 on http://pubs.rsc.org | doi:10.1039/C2SM07231A spectrometer. The optical absorption spectra of the samples were obtained at 378–278 K using a UV-vis spectrophotometer (Hitachi U-2900). All fluorescence spectra were recorded with a 378–278 K in RF-5301PC spectrophotometer.

Preparation, TEM and SEM observations

For transmission electron microscopy (TEM), a piece of the gel was placed on a carbon-coated copper grid (400 mesh) and removed after one min, leaving some small patches of the sample on the grid. The specimens were examined with a JEOL JEM-2010 transmission electron microscope operating at 200 kV using an accelerating voltage of 100 kV and a 16 mm working distance. Scanning electron micrographs of the samples were taken with a field emission scanning electron microscope (FE-SEM, Philips XL30 S FEG). The accelerating voltage of the SEM was 5–15 kV and the emission current was 10 µA.

Fluorescence lifetime microscopy (FLM) measurements

Fluorescence lifetime images were acquired by an inverse timeresolved fluorescence microscope, MicroTime-200 (PicoQuant GmBH). The excitation wavelength, the spatial resolution, and the time resolution were 375 nm, 0.3 μ m and 60–70 ps, respectively. The samples were prepared on one side of microscope cover glasses. The manufacturer's software was used to analyze the data and calculate the lifetime maps.

Rheological measurements

The rheological properties were observed on freshly prepared gels using a controlled stress rheometer (AR-2000ex, TA Instruments Ltd, New Castle, DE, USA). Cone type geometry of 40 mm diameter was employed throughout. Dynamic oscillatory work kept a frequency of 1.0 rad s⁻¹. The following tests were performed: increasing the amplitude of oscillation up to 100% apparent strain on shear, time and frequency sweeps at 25 °C (60 min and from 0.1–100 rad s⁻¹, respectively), and a heating run up to 90 °C at a scan rate of 1.0 °C min⁻¹. Unidirectional shear routines were performed at 25 °C covering a shear-rate regime between 10^{-1} and 10^3 s⁻¹. Mechanical spectroscopy routines were completed with transient measurements. In doing so, the desired stress was applied instantaneously to the sample and the angular displacement was monitored for 60 min (retardation curve).

Photophysical studies

UV-Vis absorption and emission spectra of the gel were observed at room temperature and in the range 200–800nm. The absorption properties of gel 1 were studied extensively. UV-vis absorption spectra of gel 1 (20 mM) were observed in the presence of Zn^{2+} (0–2.0 equiv).

Gelation test

Gels were prepared by dissolving 3.0 percent by weight of 1-2 in organic solvents. To this solution 2.0 equivalents of metal ion in organic solvents were added with respect to the ligand concentration. The samples were then left to stand, typically for a week.

The formation of the gel states was found to depend on the concentration of metal salt added.

Preparation of ligand 1

A mixture of 1,2,4,5-tetracyanobenzene (3) (1 g, 5.61mmol), NaN₃(4.38 g, 67.38 mmol), and triethylamine hydrochloride (9.27 g, 67.38 mmol) in 100 mL of toluene and 10 mL of methanol was refluxed for 4 days. The precipitate was then collected by hot filtration and dissolved in aqueous NaOH (1 M). The resulting clear, colorless solution was titrated with HCl (1 M) until the pH of the solution was 4. The ensuing white precipitate was washed with successive aliquots of distilled water and diethyl ether to afford 1.8 g (91.8%) of product. ¹H NMR (300 MHz, DMSO-d₆): δ 9.20 (s, 2H, CH), 5.89 (s, 4H, NH); ¹³C NMR(75 MHz, DMSO-d₆): 156.4, 132.4, 126.2 ppm; IR (KBr, cm⁻¹): 3431, 3050, 3016, 2957, 2923, 2885, 2839, 2796, 2771, 2717, 1854, 1637, 1567, 1486, 1438, 1392, 1359, 1292, 1269, 1235, 1228, 1173, 1147, 1087, 1045, 1022, 999, 934, 841, 786, 711, 653, 575, 508; MS (FAB): $352.15 (M + H)^+$ (calcd MW = 351.11); elemental analysis: calcd (%) for C₁₀H₆N₁₆: C 34.29, H 1.73, N 63.98; found: C 34.36, H 1.75, N 64.32.

Preparation of ligand 2

Compound **2** was prepared as described previously.²⁷ ¹H NMR (300 MHz, DMSO-d₆): δ 8.12 (s, 4H, CH), 4.58 (s, 4H, NH); ¹³C NMR (75 MHz, DMSO-d₆): 156.4, 132.4, 126.2 ppm; IR (KBr, cm⁻¹): 3534, 3373, 3179, 3116, 3073, 3055, 3037, 3002, 2946, 2913, 2882, 2844, 2829, 2798, 2764, 1666, 1636, 1618, 1581, 1570, 1560, 1526, 1449, 1407, 1380, 1274, 1251, 1213, 1162, 1143, 1127, 1105, 1083, 1028, 1012, 998, 911, 853, 781, 742, 630, 530, 484, 419, 409; MS (FAB): 214.07 (M - H)⁻ (calcd MW = 213.08); elemental analysis: calcd (%) for C₈H₆N₈: C 44.86, H 2.82, N 52.32; found: C 44.92, H 3.12, N 52.46.

Results and discussion

Ligands 1 and 2 were conveniently prepared in a one pot synthesis according to methods described previously (Scheme 1). Tetracyanobenzene or dicyanobenzene was reacted with sodium azide in the presence of triethylammonium chloride in toluene and ethanol to yield 1 or 2, as confirmed by ¹H and ¹³C NMR spectroscopy.



Scheme 1 Synthetic routes of ligands 1 and 2.

A coordination polymer gel based on 1 was prepared by dissolving one percent by weight of 1 in organic solvents. To this solution a small volume of metal ions in organic solvents was added in concentrations varying from 0.1-2.0 equivalents with respect to the ligand concentration. The samples were then left to stand for a week, since some gels can change into solution or precipitate. Table 1 and S1 (ESI[†]) summarize the results of a gelation test of 1 and 2 in the presence of transition metal ions (2.0 equivalents) with selected solvents. Translucent gel 1 was obtained with Zn²⁺, Cu²⁺ and Co²⁺ ions in DMF, DMA, or DMF/MeOH (Fig. 1). On the other hand, ligand 1 in the absence of metal ions did not form a gel in organic solvents or water. In addition, 1 can also be gelated with a variety of zinc counter ions such as ClO₄⁻, OAC⁻, Cl⁻, Br⁻, and I⁻ (Fig. S1, ESI⁺), indicating that the coordination polymer gel formation of 1 does not strongly depend on the nature of the anion. On the other hand, 2, possessing two tetrazole moieties did not form a gel in the presence of Zn²⁺, Cu²⁺ or Co²⁺ ions in organic solvents (Fig. S2, ESI[†]). These findings suggest that the numbers of the tetrazole moieties are important to form the coordination polymer structure.

The morphology of the xerogels obtained with different cations and anions was investigated by scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The SEM images of Zn^{2+} coordination polymer gel 1 clearly displayed a nanospherical structure with 30–50 nm in diameters (Fig. 2 and S3, ESI†). The SEM image of the Zn^{2+} coordination polymer gel 1 with different anions showed a similar nanospherical structure with 30–50 nm in diameters. In addition, the coordination polymer gel 1 formed with other cations such as Co^{2+} , and Cu^{2+} showed a similar nanospherical structure (Fig. S4, ESI†). These findings suggest that the morphology of the coordination polymer gel 1 was not strongly influenced by the nature of the cation and anion.

We examined the absorption and fluorescence emission properties of sol 1 and coordination polymer gel 1 with metal ions. The UV-vis absorption band of Zn^{2+} coordination polymer gel 1 appeared at 410 nm (Fig. 3A), indicating a typical $\pi-\pi^*$ transition.^{13,30} On the other hand, the $\pi-\pi^*$ absorption band of

Table 1 Gelation test of ligand 1 with metal ions (2.0 equiv) in organic solvents^a

Entry	Solvent	$Zn(ClO_4)_2$	$Cu(ClO_4)_2$	Co(ClO ₄) ₂
1	MeOH	PG	Р	G
2	DMF	G	G	Ğ
3	DMSO	S	G	S
4	DCM	Р	Р	Р
5	THF	PG	Р	Р
6	Toluene	Р	Р	Р
7	ACN	Р	Р	Р
8	DMA	G	G	G
9	EA	Р	Р	Р
10	CHCl ₃	Р	Р	Р
11	Dioxane	Р	Р	Р
12	H ₂ O	Р	Р	Р
13	Acetone	Р	Р	Р
14	DMF:MeOH	G	Р	G
15	DMF:H ₂ O	PG	Р	Р
^{<i>a</i>} pG: pa	artially gel, P: preci	pitate, G: stable	gel.	



Fig. 1 Photographs of the coordination polymer gel 1 with Zn^{2+} in; (a) MeOH, (b) DMF, (c) DMSO, (d) DCM, (e) THF, (f) toluene, (g) acetonitrile, (h) DMA, (i) EA, (j) CHCl₃, (k) dioxane, (l) H₂O, (m) acetone, (n) DMF:MeOH (1 : 1 v/v) and (o) DMF:H₂O (1 : 1 v/v).

sol 1 exhibited a 90 nm blue shift. The fluorescence spectra of the coordination polymer gel 1 ($\lambda_{ex} = 410$ nm) were also obtained. As shown in Fig. 3B, Zn²⁺ coordination polymer gel 1 exhibited a strong blue emission with a maximum at $\lambda = 475$ nm. The fluorescence intensity is enhanced markedly as compared to sol 1 $(\lambda_{ex} = 320 \text{ nm})$. The photoluminescence of Zn^{2+} coordination polymer gel 1 can be seen by the naked eye under UV light (Fig. 3C). Conversely, solid ligand 1 without Zn²⁺ did not show emission at any wavelength (Fig. S5). Therefore, the strong emission of gel 1 with Zn2+ originates from the self-assembled supramolecular structure formed through strong intermolecular forces and not from the monomeric ligand 1. Furthermore, in the gel state, the coordination polymer structure of 1 with Zn²⁺ plays an important role in favoring J-type aggregation, which restricts the formation of the excimer complex.³¹ We also observed the absorption and emission spectra of gel 1 with Zn2+ as obtained from DMF and DMA as shown in Fig. S6 (ESI[†]). The absorption and emission properties of gel 1 with Zn²⁺ from DMF and DMA were similar to that obtained from DMF:MeOH.

While we tried for a long time to obtain single crystals suitable for X-ray analysis in CH₃CN, the single crystal of 1 in complex with Zn²⁺ could not be attained. Therefore, molecule 1 in the aggregated gel state is likely to show dramatically enhanced fluorescence emission compared to that of the isolated state due to the synergistic effect of intramolecular planarization and restricted excimer formation. The fluorescence emission of Zn²⁺ coordination polymer gel 1 with different anions was also observed. The fluorescence intensities of Zn²⁺ coordination polymer gel 1 with ClO₄⁻, Cl⁻ and I⁻ were almost the same (Fig. S7, ESI⁺). In contrast, the fluorescence emission intensity of Zn²⁺ coordination polymer gel 1 with I⁻ decreased considerably as compared to the emission of coordination polymer gel 1 induced by other anions, due to the intersystem crossing effect.

To better understand the molecular structure of $[Zn(1)(MeOH)(DMF)]^{2+}$, we have carried out density functional theory (DFT) calculations using the nonlocal density functional of Becke's three parameters employing Lee–Yang–Parr exchange



Fig. 2 SEM images of Zn^{2+} coordination polymer gels 1 with different anions (2.0 equiv) such as (A) ClO_4^- , (B) I⁻ and (C) Cl⁻ in DMF:MeOH (1 : 1 v/v).



Fig. 3 (A) UV-vis and (B) fluorescence spectra (excitation at $\lambda = 320$ nm for sol **1** and 410 nm for gel **1**) of (a) sol **1** (20 mM) and (b) gel **1** (20 mM) with Zn(ClO₄)₂ (2.0 equiv) in DMF/MeOH (1 : 1 v/v). (C) The photograph of coordination polymer gel **1** with Zn(ClO₄)₂ without (a) and with (b) irradiation of UV light.

functional (B3LYP) with 6-31G* basis sets using a suite of Gaussian 09 programs.³² In the optimized structure of $[Zn(1)(MeOH)(DMF)]^{2+}$, Zn^{2+} is octahedrally coordinated by four tetrazole moieties of the ligand 1, DMF, and MeOH (Fig. 4). The distances between Zn²⁺ and coordinated nitrogen atom of the ligand 1 were calculated to be in the range 2.189 \sim 2.333 Å, while those between Zn²⁺ and the oxygen atom of DMF and MeOH were calculated to be 1.985 and 2.106 Å. In contrast to a previous report,33 two Br- are replaced with two tetrazole moieties of ligand 1. As the ligand 1 is replaced, the intermolecular H-bonds are generated between four tetrazole moieties of the ligand 1. It is worth noting from the structure that two intermolecular H-bonds exist between neighboring tetrazole moieties of ligand 1, rendering a total of eight H-bonds (N···H-N) in one unit structure. The H…N distances for the inner side H-bonds were calculated be in the range 1.844~2.009 A, while those in outer side were calculated to be slightly longer, in the range 1.930~2.047 Å.

Fig. 5 shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of $[Zn(1)(MeOH)(DMF)]^{2+}$. The UV-vis absorption of the assembled structure of $[Zn(1)(MeOH)(DMF)]^{2+}$ was experimentally determined to have a λ_{max} at 440 nm. The electrons in the HOMO are degenerated over ligand 1 and Zn^{2+} , while the electrons in LUMO are distributed over ligand 1. From the HOMO and LUMO, it is expected that the optical transition is contributed by the π - π * transition of ligand 1 as well as by the metal-to-



Fig. 4 The B3LYP/6-31G* optimized structure of $[Zn(1)(MeOH)(DMF)]^{2+}(H-bonds are denoted as a dotted green line).$



Fig. 5 The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of $[Zn(1)(MeOH)(DMF)]^{2+}$.

ligand charge transfer (MLCT), which is consistent with the experimentally observed transition property.

We also observed the changes in the fluorescence intensities of the gel 1 at different concentrations of Zn^{2+} . The fluorescence intensity of Zn²⁺ coordination polymer gel 1 gradually increased with the addition of Zn²⁺ until reaching the maximum fluorescence emission upon the addition of 1.0 equivalent of metal ion; the maximum emission remained almost constant upon further addition (Fig. S8, ESI[†]). Furthermore, we prepared a precipitate of 1 by the addition of an excess of Zn^{2+} (2.0 equivalents) to probe the stoichiometry in acetone or acetonitrile, since precipitated 1 complex with Zn2+ will form in acetone or acetonitrile as shown in Table 1. To remove uncoordinated Zn²⁺, the solid product was washed with aqueous solution. The solid sample, containing ligand 1 and Zn(ClO₄)₂, was examined by elemental analysis and ICP analysis. Elemental analysis and ICP of the precipitated sample demonstrated a content profile of 15.57% for C, 1.53% for H, 25.32% for N and 7.51% for Zn²⁺. Our DFT calculations also showed the following results, which are in excellent agreement with the experimental data: calculated C(16.00%), H(1.56%), O(17.88%), N(25.05%), $Zn^{2+}(7.31\%)$. These findings indicate that the stoichiometry of the sample is consistent with a 1:1 formulation.

Fluorescence of the coordination polymer gel 1 was measured as a function of temperature (Fig. S9, ESI[†]). No significant spectral changes were observed until 55 °C. The fluorescence intensity of Zn²⁺ coordination polymer gel 1 with ClO₄⁻ slightly decreased at 60 °C. Further increases in temperature resulted in a large reduction in emission. These results suggest that the emission of the coordination polymer gel 1 decreased as it started to melt at 60-65 °C. The decreasing fluorescence intensity of gel 1 above 62 °C is due to this transformation to a solution phase. The optimal emission of 1 therefore occurs when the gel is completely formed and decreases as the gel melts at higher temperature. This striking observation may be attributed to the rigidification of the media upon gelation, a process that slows down nonradiative decay mechanisms, leading to luminescence enhancement. Though the gel dissociates from the aggregated state and shows a drastic drop in fluorescence intensity, the complex still exhibits a considerable blue emission in the solution state. This may be due to weak supramolecular interactions that persist in the solution state.

To gain information about the thermally promoted stability of Mg^{2+} coordination polymer gel 1, the transition temperature $(T_{sol-vel})$ of coordination polymer gel 1 was measured by

differential scanning calorimetry (DSC) (Fig. S10, ESI[†]). The Zn²⁺ coordination polymer gel **1** reveals a sharp phase transition at 62 °C, indicative of an endothermic reaction. This endothermic thermogram is due to Zn²⁺ coordination polymer gel **1** changing into a sol state as seen in Fig. S9 (ESI[†]). This sol–gel transition temperature of Zn²⁺ coordination polymer gel **1** is consistent with the results obtained by fluorescence spectroscopy.

The luminescence property of Zn²⁺ coordination polymer gel 1 was studied by time-resolved fluorescence confocal microscopy. The emission decay profile was monitored over the range $\lambda =$ 405-490 nm for Zn²⁺ coordination polymer gel 1 (Fig. S11, ESI[†]). The fluorescence decay of Zn²⁺ coordination polymer gel 1 was fitted with a single exponential component yielding a lifetime of 3.36 ns (Fig. S11B-a), indicating that this emission is fluorescence. In addition, the fluorescence intensity of Zn²⁺ coordination polymer gel was more than 1000 times higher than that of the ligand 1 alone. This result reflects the fact that coordination polymer gel 1 in its aggregate state is more rigid, restricting the rotational and vibrational movements of molecules. In contrast, the fluorescence lifetime of solid 1 was less than 2.0 ns (Fig. S11Bb). The limited molecular motions decrease the nonradiative relaxation process, which leads to the longer lifetime and fluorescence enhancement.34

Rheological information is an indicator of the behavior of the gels when they are exposed to mechanical stress, especially the "storage" (or "elastic") modulus G', which represents the ability of the deformed material to "snap back" to its original geometry, and the "loss" (or "viscous") modulus G', which represents the tendency of a material to flow under stress. Two rheological criteria required for a gel are: (i) the independence of the dynamic elastic modulus, G', with respect to the oscillatory frequency, and (ii) G' must exceed the loss modulus G'' by about 1 order of magnitude.

We first used dynamic strain sweep to determine the proper condition for the dynamic frequency sweep of the gel at different concentration of Zn^{2+} . As shown in Fig. 6A, the values of the storage modulus (G') and the loss modulus (G') exhibited a weak dependence from 0.1 to 1.0% of stain (with G' dominating G''), indicating that the sample is a gel. The values of both G' and G'' of the gel in the presence of 1.0 equivalents of Zn^{2+} dramatically increased in comparison to the gels in the presence of only 0.3 or 0.6 equivalents of Zn^{2+} . These results reflect that the gel was stabilized with almost complete coordination polymer structure in the presence of 1.0 equivalents of Zn^{2+} , because ligand 1 forms a 1 : 1 complex with Zn^{2+} .

We used dynamic frequency sweep to study the gel after setting the strain amplitude at 0.8% (within the linear response region of the strain amplitude). Fig. 6B exhibits that G' and G'' are almost constant with the increase of frequency from 0.1 to 100 rad s⁻¹. The value of G' is about 10 times larger than that of G'' over the whole range (0.1–100 rad s⁻¹), suggesting that the gel is fairly tolerant to external force. As observed by changes of dynamic strain sweep, the values of both G' and G'' of the gel at values above 1.0 equivalent of Zn²⁺ concentration was 10 time larger than that of the gel in the presence of 0.3 equivalent of Zn²⁺.

Furthermore, time-dependent oscillation measurements were used to monitor the gelation process of Zn^{2+} coordination polymer gel **1**, which forms gradually upon mixing of ligand **1** and Zn^{2+} (Fig. S12, ESI[†]). The time sweep shows the rapid



Fig. 6 Dynamic oscillatory and steady shear measurements of coordination polymer gel **1** at different concentration of Zn^{2+} at 25 °C: (A) strain sweep at a frequency of 1 rad s⁻¹; (B) frequency sweep at a strain of 0.01%; **1**:Zn(ClO₄)₂ = 1 : 0.3 **•**: G', **•**: G''; **1**:Zn(ClO₄)₂ = 1 : 0.6 \triangle : G', \diamond : G''; **1**:Zn(ClO₄)₂ = 1 : 1 G': **•**, **v**: G''; **1**:Zn(ClO₄)₂ = 1 : 2 \Rightarrow : G', \bigcirc : G''.

growth of G' and G'' in the initial stage of gelation, followed by a slower long term approach to a final pseudo-equilibrium plateau. At the end of the experiment, the value of G' was about an order of magnitude higher than G''. All values of G' and G'' in the coordination polymer gel are strongly influenced by the concentration of the ligand 1 complex with metal ions.

Conclusions

We have reported the formation of a simple Zn²⁺-based coordination polymer gel. A tetrazole-appended ligand was shown to efficiently produce an organogel by simple mixing with Zn²⁺. Photophysical studies showed that the coordination polymer gel exhibited a typical π - π * transition and gave rise to highly fluorescent behavior. Upon the formation of the coordination polymer gel, the complex shows a pronounced fluorescence enhancement with a long lifetime, as compared to the ligand. The rheological properties of the Zn²⁺-tetrazole coordination polymer gel were strongly dependent on the concentration of Zn²⁺. The tetrazole-based ligand 1 complex with Zn²⁺ was strongly influenced to the concentration of metal ions to form the 3D coordination polymer structure. The present results emphasize the validity of ligand design that includes anion- and metalbinding in realizing gel systems with very versatile and stimuliresponsive properties. These concepts should open the door for a wide range of responsive soft materials.

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