PAPER

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A metal–organic framework gel with Cd²⁺ derived from only coordination bonds without intermolecular interactions and its catalytic ability[†]

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A cyclohexane-based ligand (1) as a triconnected linker forms a supramolecular gel in the presence of transition metal ions, particularly Cd^{2+} and Zn^{2+} . 1 can also be gelated with cadmium counter ions such as NO_3^- , ClO_4^- and SO_4^{2-} . The gels have been characterized by SEM, TEM, rheometry and single crystal X-ray crystallography. The Cd^{2+} -cyclohexane-based ligand gel shows a fibrillar structure with diameters ranging from 20–50 nm. X-ray analysis revealed that 1 forms a 1D coordination polymer structure with the Cd^{2+} ion, with an octahedral structure. The rheological properties of the Cd^{2+} -cyclohexane-based ligand gel were strongly dependent on the concentration of Cd^{2+} . Furthermore, the xerogel 1 with Cd^{2+} acted as a base catalyst in the Knoevenagel condensation reaction.

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Introduction

Organogels and hydrogels composed of small molecules or 'low molecular weight gelators' (LMWGs) which are linked into fibers by supramolecular interactions are current topics 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.¹⁻²² 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,^{23,24} catalytic action,^{25,26} absorption,^{27,28} emission,²⁹⁻³² magnetism²⁸ and electron emission.²⁶ 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. In general, the organic ligands form the gel in the presence of metal ions by the intermolecular interactions such as H-bonds, π - π stacking and van der Waals interactions.²³⁻³² Metalorganic framework gels (MOFGs) with amide moieties are candidate compounds that have functional organic sites as guest interaction

sites.³³ The amide group is a versatile functional group because it can participate in two types of intermolecular hydrogen-bonding interactions: the -NH moiety acts as an electron acceptor and the -C=O group acts as an electron donor.³⁴ These multifunctional moieties of amide groups tend to form hydrogen bonds among themselves and interact negligibly with guest molecules after formation of MOFGs. If MOFGs could be prepared without forming amide-amide interactions, these groups would constitute attractive interaction sites for selective sorption, reaction and/or catalysis on the surface of the gel. To retain amide groups as guest-interaction functional organic sites in the network, we employed a threeconnector ligand, 1,3,5-cyclohexane tricarboxylic acid tris[N-(4pyridyl)amide], containing three pyridyl groups as coordination sites and three amide groups as guest interaction sites. Herein, we describe an approach for the preparation of a MOFG with Cd²⁺ using base-type functional organic sites and demonstrate its base catalytic properties in a heterogeneous reaction. The coordination structure of a MOFG with Cd²⁺ was proven by single X-ray crystallography. Furthermore, the rheology of a MOFG with Cd²⁺ exhibited the behavior of a typical organogel.

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Results and discussion

Ligand **1** was conveniently prepared in a one pot synthesis according to methods described previously (Scheme 1). **1**,3,5-Cyclohexane tricarboxytrichloride was reacted with 4-aminopyridine in the presence of triethylamine in THF to yield **1**, as confirmed by ¹H, ¹³C NMR, mass spectroscopy and elemental analysis.

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 Table 1
 Gelation test of ligand 1 with metal ions (3.0 equiv.) in organic solvents and water

Entry	Solvent	$ZnSO_4$	$CdSO_4$
1	МеОН	Р	Р
2	DCM	Р	Р
3	TKF	Р	Р
4	Toluene	Р	Р
3	AN	Р	Р
6	EA	Р	Р
7	CHC1 ₃	Р	Р
8	Ethanol	Р	Р
9	H_2O	G	G
10	DMF	S	S
11	DMSO	S	S
12	H ₂ O: DMSO	Р	Р

A coordination polymer gel based on 1 was prepared by dissolving 1% (by weight) of 1 in water. To this solution a small volume of metal ions in water was added in concentrations varying from 1.0–4.0 equivalents with respect to the ligand concentration. The samples were then left to stand for a week. Table 1 and Table S1 in ESI[†] (abbreviated as S), summarize the results of a gelation test of 1 in the presence of transition metal ions (2.0 equivalents) with water. Opaque gel 1 was obtained with Cd²⁺ and Zn²⁺ ions in water (Fig. 1). In addition, 1 can also be gelated with a variety of cadmium counter ions such as NO₃⁻, ClO₄⁻ and SO₄²⁻, but 1 could not gelate when the counter ion was Cl⁻, Br⁻ and I⁻ (Fig. 2), because the Hofmeister effects of NO₃⁻, ClO₄⁻ and SO₄²⁻ are much weaker than those of Cl⁻, Br⁻ and I⁻. The weak Hofmeister effect of anions did not induce gelation, due to high solubility in water.

The morphology of xerogels obtained with different cations and anions was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM images of Cd^{2+} coordination polymer gel **1** clearly displayed a fibrillar structure with diameters of 10–20 nm and several



Fig. 1 Photographs of 1 with (a) CdSO₄, (b) ZnSO₄, (c) CuSO₄, (d) CoSO₄, (e) NiSO₄ and (f) MnSO₄ in H₂O.



Fig. 2 Photographs of **1** with; (a) $CdSO_4$, (b) $Cd(NO_3)_2$, (c) $Cd(CIO_4)_2$, (d) $CdBr_2$, (e) $CdCl_2$ and (f) Cdl_2 in H_2O .



Fig. 3 (a) SEM and (b) TEM image of Cd^{2+} coordination polymer gel 1.

micrometers in length (Fig. 3 and Fig. S1, ESI[†]). The SEM image of Cd^{2+} coordination polymer gel **1** using different anions showed a similar fiber structure with diameters of 10–20 nm.

The gelation abilities of 1 were tested with other cations such as Zn^{2+} , Co^{2+} and Cu^{2+} under the same conditions. Upon the addition of Zn²⁺ the gel formation was induced (Fig. S2, ESI⁺), whereas upon addition of Co²⁺ and Cu²⁺ no gel formation occurred. It is known that Cd²⁺ and Zn²⁺ ions have octahedral structures with ligands. Therefore, the octahedral coordination polymer structure of 1 with metal ions could be gelatized in a solvent. These findings suggest that the gel formation of 1 is influenced by the coordination structure of the cations. We examined the absorption and fluorescence emission properties of sol 1 and coordination polymer gel 1 with metal ions. The UV-vis absorption bands of Cd²⁺ coordination polymer gel 1 and sol 1 appeared at 262 nm (Fig. S3, ESI[†]), indicating that the gelator **1** in the gel state did not undergo the π - π * transition. The coordination polymer gel **1** with Cd²⁺ exhibited no emission (Fig. S3, ESI⁺). Therefore, the formation of the coordination polymer gel 1 originated from the coordination bond between the gelator 1 and Cd²⁺, but was not due to intermolecular interactions such as π - π stacking, H-bonds, and van der Waals forces.

To better understand the molecular structure of gel **1** with Cd^{2+} , we prepared a single crystal of **1** with Cd^{2+} by reacting **1** with cadmium sulfate in a dichloromethane–methanol mixture in the presence of a small amount of HCl, which yielded a colorless precipitate. Vapor diffusion of diethyl ether into a DMF solution of this complex gave crystalline **1a** (Tables S2 and S3, ESI†). X-Ray analysis revealed that **1a** is a 1D coordination polymer with the formula { $[Cd(H1)_2(SO_4)_2]$ ·DMF·4H₂O}_n as shown in Fig. 4. The Cd(π) center is octahedrally coordinated to the pyridyl nitrogen atoms from different bridging (**1**) and two



Fig. 4 Single crystal structure of 1a ({[Cd(H1)₂(SO₄)₂]·DMF·4H₂O}_n)



Fig. 5 Powder X-ray diffraction patterns of (a) crystal 1 with CdSO₄ and xerogel 1 with (b) CdSO₄ and (c) Cd(NO₃)₂.

oxygen atoms from sulfate anions by twofold rotation symmetry (C2 axis) through Cd(II). In addition, an acidic proton protonates N4 in the presence of a small amount of HCl as solvent.

Wide-angle X-ray diffraction (WAXD) was used to probe the molecular packing of gel 1 with the cadmium ion. Powder XRD patterns of ligand 1 with CdSO₄ in the bulk crystal had the same diffraction pattern as that of the xerogel 1 with CdSO₄. Furthermore, the strong similarities between the powder XRD patterns of the xerogel 1 with CdSO4 and those with other counter ions such as ClO₄⁻ and NO₃⁻ suggested that the molecular packing of the gel 1 with SO_4^{2-} as the counter ion was the same as the molecular packing of the gel 1 with other counter ions (Fig. 5).

To garner an insight into the thermally promoted stability of Cd²⁺ coordination polymer gel 1, the transition temperature $(T_{\text{sol-gel}})$ of coordination polymer gel **1** was measured using differential scanning calorimetry (DSC) (Fig. S4, ESI⁺). Cd²⁺ coordination polymer gel 1 showed a sharp phase transition at 115 °C, undergoing an endothermic reaction. This endothermic thermogram is due to the transition of the Cd²⁺ coordination polymer gel 1 into a solution phase (Fig. S4, ESI⁺).

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 conditions for the dynamic frequency sweep of the gel at different concentrations of Cd^{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 strain (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 3.0 equivalents of Cd²⁺ dramatically increased in comparison to the gels in the presence of only 2.0 equivalent of Cd²⁺. These results reflect that the gel was stabilized with an almost complete coordination polymer structure in the presence of 3.0 equivalents of Cd²⁺.

We used dynamic frequency sweep to study the gel after setting the strain amplitude at 0.08% (within the linear response region of the strain amplitude). G' and G'' were almost constant with the increase of frequency from 0.1 to 100 rad s^{-1} (Fig. 6b). The value of G' was 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 in dynamic strain sweep, the values of both G' and G'' of the gel at values above 3.0 equivalents of Cd^{2+} concentration were larger than that of the gel in the presence of only 2.0 equivalent of Cd²⁺. Furthermore, time-dependent oscillation measurements were used to monitor the gelation



Fig. 6 (a) Strain sweep at a frequency of 1 rad s⁻¹ of the Cd²⁺ coordination polymer gel 1. (b) Frequency sweep of G' and G'' for the Cd²⁺ coordination polymer gel 1 at a strain of 0.01%. (c) Time sweep of G' and G'' for the Cd²⁺ coordination polymer gel **1** at a strain of 0.01% and a frequency of 1 rad s⁻¹ (2 equiv.: G': \diamond , G'': \bigcirc , 3 equiv.: G': ◆, G'': ●)

process of gel **1** with Cd^{2+} (Fig. 6c). The time sweep shows the rapid increase 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 **1** with Cd^{2+} .

To characterize the base-type properties of xerogel 1, we performed a Knoevenagel condensation reaction catalyzed by xerogel 1. The Knoevenagel reaction is well known, not only as a weak base-catalyzed model reaction but also as a reaction that generates a C-C bond. Knoevenagel condensation reactions of benzaldehyde with each of the active methylene compounds (malononitrile, ethyl cyanoacetate and cyano-acetic acid tertbutyl ester) were catalyzed by xerogel 1. The conversion yields of the respective adducts were obtained as follows: 80% for malononitrile, 73% for ethyl cyanoacetate and 75% for cyanoacetic acid tert-butyl ester. The results indicate that the reaction mainly occurred on the surface of xerogel 1. The heterogeneity and recyclability of xerogel 1 in the Knoevenagel condensation of benzaldehyde and malononitrile were also examined. The catalyst ability of xerogel 1 showed good recyclability. In addition, xerogel 1 is easily isolated from the reaction suspension by filtration alone and can be reused without loss of activity.

Conclusions

We have reported the formation of a simple MOF-based gel with Cd^{2+} . A cyclohexane-based ligand as a triconnected linker efficiently produced the hydrogel by simple mixing with Cd^{2+} and Zn^{2+} . The ligand **1** forms a coordination polymer structure based on the octahedral Cd^{2+} center. The rheological properties of the Cd^{2+} -cyclohexane-based ligand gel were dependent on the concentration of Cd^{2+} . Furthermore, the amide groups of gel **1** acted as a base-catalyst in the Knovenagel condensation reaction. This research is particularly relevant in the context of MOF-type gel chemistry in the generation of new materials with unusual properties. The present results also suggested that the combination of metal ions and a designed ligand can provide a MOF-type gel with functional organic sites that show base-catalytic performance.

Experimental

General

All reagents were purchased from Aldrich and Tokyo Kasei Chemicals and used without further purification. ¹H and ¹³C NMR spectra were measured using a Bruker ARX 300 apparatus. IR spectra were obtained for KBr pellets, in the range 400–4000 cm⁻¹, with a Shimadzu FT-IR 8400S instrument, fluorescence spectra were recorded on a RF-5301PC spectrophotometer and mass spectra were obtained using a JEOL JMS-700 mass spectrometer. The optical absorption spectra of the samples were obtained at 25 °C using a UV-vis spectrophotometer (Hitachi U-2900). In addition, X-ray diffraction patterns of MOFG and crystal sample were measured using a Rigaku diffractometer (Type4037) using graded *d* space elliptical side-by-side multilayer optics, monochromated Cu K radiation (40 kV, 30 mA) and an imaging plate (R-AxisIV).

Preparation for 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 using 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 micro-graphs of the samples were taken with a field emission scanning electron microscope (FE-SEM, Philips XL30 S FEG). The accelerating voltage for SEM was 5–15 kV and the emission current was 10 µA.

DSC measurement. Differential scanning calorimetry (DSC) was performed on a Seiko DSC6100 high-sensitivity differential scanning calorimeter equipped with a liquid nitrogen cooling unit. Samples of gels were hermetically sealed in a silver pan and measured against a pan containing alumina as the reference. The thermograms were recorded at a heating rate of 0.5 $^{\circ}$ C min⁻¹.

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 maintained 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 10³ 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 gels were observed at room temperature and in the range of 200–800 nm. The absorption properties of gel **1** with Cd^{2+} were studied extensively. UV-vis absorption and fluorescence spectra of gel **1** (0.01 mM) were observed in the presence of Cd^{2+} (1.0–4.0 equiv.).

Gelation test. Gels were prepared by dissolving one percent by weight of **1** in water. To this solution a small volume of metal ions in organic solvents was added in varying concentrations from 1.0 to 4.0 equivalents with respect to the ligand concentration. The volume of the metal salt solution was typically around 1–5 wt% of the total solution. 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.

Knoevengael condensation reaction catalyzed by MOFG with Cd^{2+} . A solution of benzaldehyde (0.21 mL, 2.1 mmol) and malononitrile (or ethylcyanoacetate or cyano-acetic acid *tert*-butyl ester) (0.132 g, 2.0 mmol) in CHCl₃ (1 mL) was stirred for 5 min. Then MOFG 1 (0.10 g, 0.08 mmol, 4 mol%) was added. The suspension was stirred at room temperature for 12 h. The progress of the reaction was monitored by ¹H NMR (CDCl₃) or gas chromatography. The catalyst was removed by filtration, washed with benzene, and recovered.

X-ray crystallography. Data were collected on a Bruker Smart APEX2 ULTRA diffractometer using a graphite monochromated Mo K α (λ = 0.71 073 Å) radiation source at 173(2) K. The frame data was processed to give structure factors using SAINT-plus.³⁵ The structure was solved by direct methods and refined by fullmatrix least-squares methods on F^2 for data using SHELXTL software.³⁶ The crystal of 1a appears to contain a certain amount of the DMF-water solvent mixture trapped in the crystal lattice in a severely disordered manner. The solvent could not be reliably modeled and therefore the SQUEEZE technique37 was used to subtract its contribution from the diffraction pattern. A SQUEEZE calculation indicated the presence of 626.7 e per unit cell with a solvent accessible area volume of 2246.1 Å in 1a. Considering the asymmetric unit, this may be attributed to one DMF and four water molecules in the crystal lattice.

Preparation of ligand 1. A solution of 4-aminopyridine (17.0 g, 18.0 mmol) and distilled triethylamine (24 mL, 18.4 mmol) in distilled THF (200 mL) was added dropwise to a solution of 1,3,5-cyclohexane tricarboxytrichloride (10 g, 18 mmol) in THF (60 mL) at 0 °C. The reaction mixture was stirred for 12 h. The temperature was allowed to step up to room temperature. The brown crude product 1 was collected by filtration and washed with THF. The product was recrystallized from methanol (200 mL) by stirring for 1 h. The white powder was collected by filtration, washed with acetone, and dried under vacuum for 1 day at room temperature (21.4 g, 30%). Mp: 327 °C. ¹H NMR (300 MHz, MeOD-d₄): 8.4–8.39 (s, CH), 7.69 (s, CH), 2.66 (s, CH₂), 2.2–2.15 (m, CH₂), 1.9–1.83 (m, CH₂); ¹³C NMR (300 MHz, DMSO-d₆): 174.4, 150.7, 146.15, 113.7, 44.0, 31.1 ppm; IR (KBr, cm⁻¹): 1669, 1591, 1506, 1413, 1381, 1328, 1302, 1250, 1210, 1169, 1001, 855, 821 cm⁻¹; MS (ESI) m/z445.17 $(M+H)^+$ calcd for $C_{24}H_{24}N_6O_3$: 444.19; anal. calcd for C₂₄H₂₄N₆O₃: C 64.85, H 5.44, N 18.91%; found: C 64.12, H 5.58, N 18.89%.

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