

Spontaneous Enrichment of Organic Molecules from Aqueous and Gas Phases into a Stable Metallogel

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This paper reports a dimethyl sulfoxide (DMSO) phase offered by a coordination polymer gel that consists of metal ions and a calixarene that has multiple binding sites. This metallogel, virtually 98% of which is DMSO, has high stability in aqueous solution over a wide range of pH (1–13), even at 100 °C, rejects ions (almost) completely, and allows nonionic organic molecules spontaneously enriching into it with high efficiency, up to ~60 times enrichment from aqueous solution and ~2000 times enrichment from the gas phase.

Introduction

This paper describes a coordination polymer gel (termed “metallogel” to emphasize the metal–ligand bond) that enriches organic molecules from aqueous and gas phases. Monitoring low-concentration hazardous organics, for example, chlorobenzene or toluene in water or polyaromatic hydrocarbons (PAHs) in air, requires an efficient sampling method to enrich those nonionic organic molecules from aqueous or gas phases. Using nonpolar solvents to extract organic hazards from water is hardly practical since most of organic solvents themselves are detrimental to the environment, and a solute at ultralow concentration makes extraction ineffectual. Nature, however, evolves a better way to overcome such an obstacle: bacteria (e.g., alkylotrophs) develop specialized cell walls that “dissolve” and accumulate hydrocarbons and transport them to catalytic sites in their cell membranes. Using such a unique arrangement, bacteria circumvent the difficulty of enzymatic attack of otherwise low-concentration alkanes in the aqueous phase.¹ Although such an uptake process is the fundamental step in the activities of the bacteria, few systems mimic that uptake process. We intend to build an artificial system to take up trace amounts of nonionic organic molecules from the aqueous phase and choose to construct such a synthetic system on dimethyl sulfoxide based gel materials.

As noncrystalline materials, gels, formed by three-dimensional, elastic polymeric networks whose interstitial spaces are filled with a fluid, not only can undergo large deformation by external stimuli^{2,3} but also allow other molecules or ions to move through or be trapped inside. They have found many useful applications: in gel electrophoresis,⁴ catalyst screening,⁵ chemical sensing,⁶ and mechanical actuation⁷ and as a reaction medium.⁸ Generally, formation of a gel utilizes one or a combination of four kinds of forces: ionic, covalent, hydrogen bond, and hydrophobic interaction. In this work, we employed metal–ligand bonds for the gel formation. Although being

used extensively in crystal engineering,^{9,10} metal–ligand bonding to form coordination polymers has been less explored in constructing gel materials.^{11,12} We believe that a combination of scaffolds that have multiple binding sites with metal ions, which possess unique electronic, magnetic, optical, geometrical, or catalytic properties, will provide a simple, versatile approach to construct gel materials with interesting behaviors and functions. A metallogel, for example, may ultimately offer a system that catalytically converts harmful organic hazards to environmentally benign compounds in aqueous phases.

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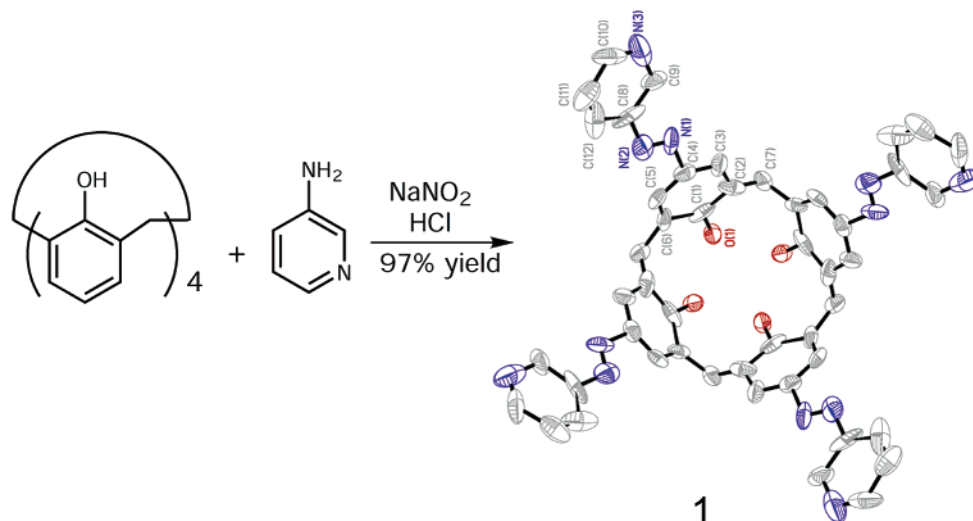


Figure 1. Synthetic route and X-ray structure of the ligand, 3-pyridine-azo-calix[4]arene (**1**).

We planned to use dimethyl sulfoxide (DMSO), an environmental friendly industrial solvent that dissolves most of the organics but is highly miscible with water, as a fluid phase of the metallogel. This fluid phase, when incorporated into a gel, should be immiscible with water and will potentially allow extraction, enrichment, detection, and conversion of organics.

Here we report such a DMSO phase offered by a coordination polymer gel^{3,6–8} that consists of DMSO, metal ions, and a tetradentate ligand: a calixarene with four binding sites.^{13–16} This metallogel, composed of 98% DMSO in weight, displays high stability in aqueous solution over a wide range of pH (1–13), even at elevated temperature. It rejects metal ions (almost) completely but allows organic molecules spontaneously enriching into it with high efficiency, up to ~60 times enrichment from aqueous solution and ~2000 times enrichment from the gas phase. Such a property may offer a new means to reduce the interferences caused by ions during the analysis of organics in marine settings. We anticipate that metallogels will find broad applications in environmental, catalysis, and separation technologies, and such a methodology will also provide a simple, easy route to explore and utilize otherwise (mostly) insoluble coordination polymers.

Experimental Section

Materials. Calix[4]arene and [Pd(ethylenediamine)]Cl₂ were obtained from Aldrich. Commercially available reagents and solvents were used without further purification, unless indicated otherwise. All the other chemicals were of reagent grade or better. The synthesized compounds were characterized using ¹H NMR (Bruker ARX 300) and elemental analysis (Perkin-Elmer 240). The concentrations of metal ions were measured using inductively coupled plasma (ICP). UV–vis spectra were performed in a Cary-5E spectrophotometer.

Synthesis of 3-Pyridine-azo-calix[4]arene (1**) and [Pd(en)(H₂O)₂](NO₃)₂.** 3-Aminopyridine (45 mg) was dissolved in a solution of 1 N HCl (1 mL) and THF (1 mL), and NaNO₂ (35 mg) was added to the solution. NaBF₄ (100 mg) was added into the solution after stirring at 0 °C for 20 min. This solution was added into a solution of calix[4]arene (50 mg) in MeOH/DMF (1:1, 1 mL) at room temperature. An orange-red solid (**1**) precipitated after 30 min and was collected by filtration, sequentially washed by water, methanol, and ethyl ether, and dried under vacuum. The final weight of the product is 97 mg (97% yield). MS for C₄₈H₃₆N₁₂O₄: M⁺ = 844; observed (M + 1)⁺ = 845. ¹H NMR (DMSO-*d*₆): δ 3.72 (brd, 4 H, CH₂), 4.42 (brd, 4 H, CH₂), 7.74 (dd, 4 H, ArH), 7.82 (s, 8 H, ArH), 8.30 (d, 4 H, ArH), 8.70 (d, 4 H, ArH), 9.07 (s, 4 H, ArH). [Pd(en)(H₂O)₂](NO₃)₂ was prepared by treating [Pd(en)Cl₂] with 1.98 equiv of AgNO₃

under light exclusion, according to a standard method. After drying under a vacuum, the yellow color diaqua complex was obtained.

UV–Vis Spectroscopy. A 4.0 mL quantity of freshly made aqueous solutions of toluene or chlorobenzene was added into a small vial containing 0.4 mL of gels (2 wt % gelator). The time acquisition spectra of UV absorbance of the toluene solution were recorded under ambient conditions.

Results and Discussion

Ligand Synthesis and Properties. A tetrameric molecule provides an easy, simple way to construct the scaffolds with multiple binding sites. We chose calix[4]arene, a cyclic molecule with four phenols bridged by methylene groups, as the framework to attach ligands since the chemistry of calixarene is well-defined and extensively developed.^{13,15,17,18} A calixarene, with multiple binding sites and conformational flexibility, will promote an effective cross-linking to form a polymeric network that is critical for gelation. The cavity of calix[4]arene will also help to “hold” the solvent molecules. Calix[4]arene itself has served as a gelator in nonpolar solvents, such as cyclohexane, hexane, and carbon disulfide,¹⁹ but has been less explored to serve as a ligand for making coordination polymer gels (metallogels).¹¹ To maximize the size of the intermolecular space and introduce the binding sites for metal ions, we synthesized 3-pyridine-azo-calix[4]arene (**1**) in 97% isolated yield, using a modified procedure^{16,17} (Figure 1).

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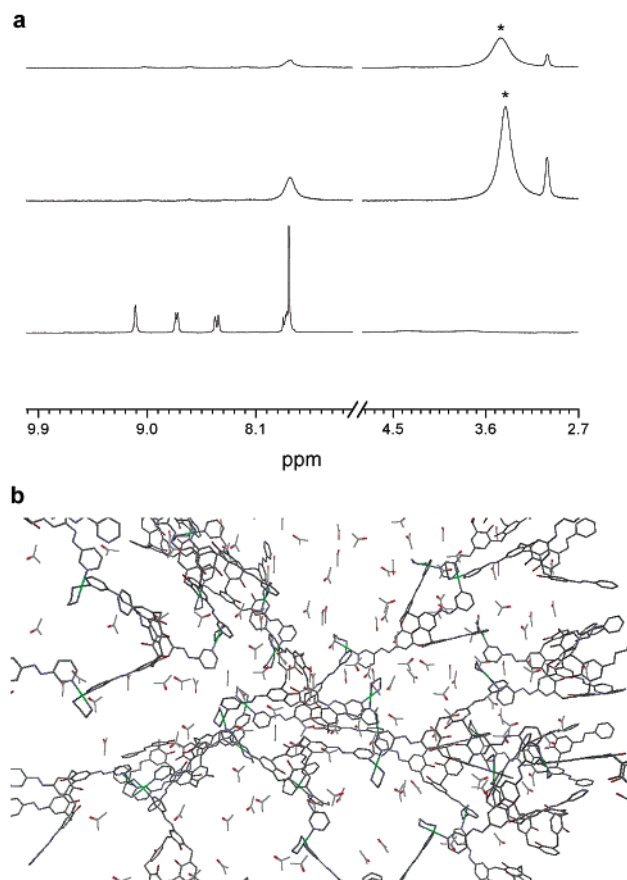


Figure 2. (a) ^1H NMR of aromatic protons and geminal protons on the methylene bridge of ligand **1** before and after gelation (H_2O peak indicated by *): free ligand (below), the coordination polymer (middle), and the metallogel (above). (b) A hypothetical microstructure of the gel: DMSO molecules fill the polymer networks that consist of different conformers of **1** linked by $[\text{Pd}(\text{en})]^{2+}$.

Compound **1** maintains a cone conformation in the crystal phase but is conformationally flexible in solution. Due to the high content of disordered solvent molecules (DMSO) in the unit cell, we were only able to determine the core structure of **1** and the space group ($P4/ncc$) of the crystal. Our preliminary X-ray analysis indicates that the angle between the opposite phenol rings (the constituents of the cone) is around 76° , and DMSO molecules fill the voids within and between the large cones of **1** and occupy about 30% of the volume of the unit cell. Compound **1** is, however, conformationally flexible at 25°C in DMSO solution as the ^1H NMR spectrum in DMSO- d_6 shows two broad peaks at 4.30 and 3.65 ppm (the bridging methylene protons of all four conformations of calix[4]arene¹⁵ interconvert) (Figure 2a). ^1H NMR study of **1** also indicates that **1** forms aggregates when its concentration reaches 0.012 M in DMSO at 25°C ; raising the temperature removes the aggregation. No gelation, however, was observed with **1** alone in DMSO, DMF, or pyridine. Although the hydrophobicity of the calix[4]arene core makes **1** insoluble in neutral water, **1** dissolves in acidic ($\text{pH} = 1$) or basic ($\text{pH} = 13$) aqueous solution, likely due to its protonatable pyridine groups and deprotonatable hydroxyl groups.

Formation of the Metallogels. We control the formation of coordination polymers and metallogels by carefully choosing metal ions, ligands, and solvents. $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2]^{2+}$ and pyridine are well-known to generate

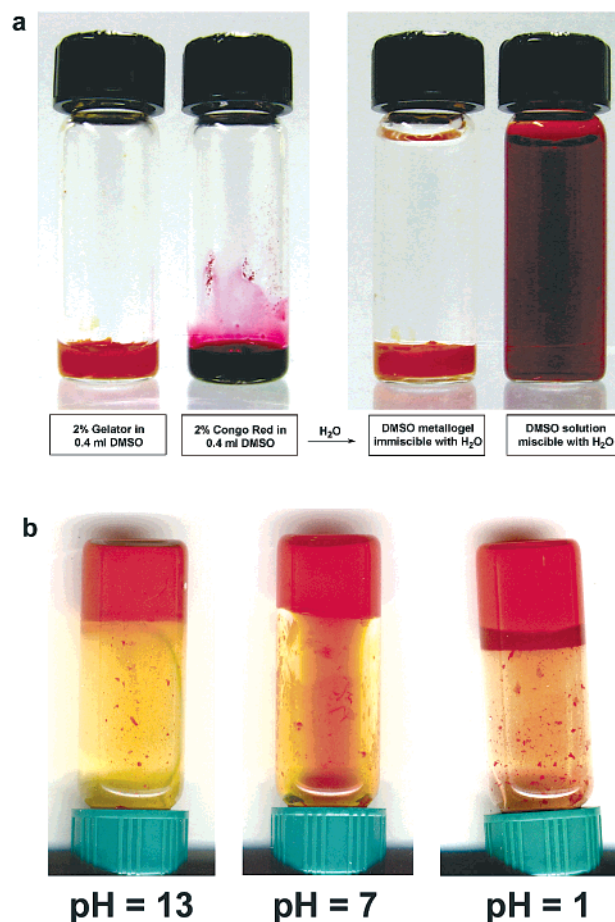


Figure 3. (a) Images of the metallogel containing 98% DMSO and a Congo Red solution containing 98% DMSO; while the latter is miscible with water, the former is not. (b) Images of the gels at different pHs.

extended molecular structures.^{10,20} We first used $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2]^{2+}$ as the source of metal ions to form a coordination polymer and monitored the formation of the polymer and the gel using ^1H NMR in DMSO- d_6 . The peaks of the aromatic protons broadened, and the broad peaks of the methylene proton at 4.30 and 3.65 disappeared immediately after adding $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ to the DMSO solution of **1**, as shown in Figure 2a. Nevertheless, the peaks of protons on the ethylenediamine shifted and broadened due to the formation of the coordination polymers. Those peaks become even broader and less intense (Figure 2a) after completed gelation; that is, gelation is confirmed by the inverted test tube method (Figure 3b). The typical mole ratios of Pd(II) to **1** are in the range of 1.8:1–2:1, and the weight percentages of the coordination polymers in the gels are in the range of 0.5%–2%, corresponding to the mole ratio of the gelator and the solvent at $\sim 1:10^3$. The typical gelation time is 4 h (from adding $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ to the solution till confirmed by inverted test tube method or NMR). Figure 2b illustrates a proposed microstructure of the metallogel: DMSO fills the interstitial space of random conformers of **1** cross-linked by the $[\text{Pd}(\text{en})]^{2+}$ ions. Figure 3a shows that 0.4 mL of this metallogel, essentially 98% DMSO, is immiscible with 4.0 mL of water. For comparison, also shown in Figure 3a is a photo of 2% Congo Red in 0.4 mL of DMSO solution, which is completely miscible with 4.0 mL of water. The orange-red color of the gel results from

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the chromogenic azo groups (Figure 3a). The electrical conductivity of the gel is $\sim 5 \times 10^{-7}$ S/cm.

It took 72 h to form the metallogel in DMSO when [Pd(COD)]Cl₂ (COD, cyclooctadiene) served as the source of the metal ions. A slower ligand-exchange process between COD and pyridine may contribute to the longer gelation time for [Pd(COD)]Cl₂, compared to that of [Pd(en)(H₂O)₂](NO₃)₂.

Stability of the Metallogels. The degree of cross-linking determines the stability of the metallogel. The formation of the gel is thermally reversible when the ratio of gelator to solvent is 0.5 wt %. Increasing the ratio of gelator to 2 wt % results in a gel that is even stable in DMSO solution upon heating or ultrasonating. This result demonstrates that more cross-linking, at a higher concentration of gelator, produces more stable gels. This gel is stable (no shrinkage or swelling observed within 72 h) in both hydrophilic solvents (for example, THF, DMF, and DMSO) and hydrophobic solvents (for example, CHCl₃, CH₂Cl₂, and toluene), even at elevated temperatures. The gel (0.4 mL) completely dissolves in pyridine (2 mL) and collapses and precipitates in 0.8 mL of acetone. The precipitated polymers do not act as a gelator when being added back into DMSO but dissolve in pyridine. Although **1** is soluble in aqueous solution at pH = 13 or pH = 1, the gel, formed by **1** and [Pd(en)(H₂O)₂](NO₃)₂ in DMSO, is insoluble and stable in water over a wide range of pH (1–13, pictures of the gels in different pHs are shown in Figure 3b), even up to 100 °C.

Enrichment of Organics from the Aqueous Phase. The hydrophobicity and stability of the gel enable it to extract organic molecules spontaneously from aqueous solution, and it enriches these molecules into its interstitial space. The extraction process was monitored using time acquisition spectra of UV absorbance of the organic substrates, and the rate of extraction and enrichment was calculated based on the decrease of the concentration of the organic substrate in the aqueous solution under ambient conditions. We added 4.0 mL of freshly made aqueous solutions of toluene ($A_{261\text{nm}} = 0.789$, 570 ppm) into a small vial (1.2 × 4.5 cm) containing 0.4 mL of gels (2 wt % gelator). As illustrated in the inset of Figure 4a, the decrease of toluene concentration in aqueous solution followed a curve of exponential decay. We also estimated the maximum amount of the enrichment of the toluene in the gel according to eq 1:

$$C_{\text{gel}} = \frac{(A_{\text{initial}} - A_{\text{final}})}{A_{\text{initial}}} C_{\text{aqueous}} \frac{V_{\text{aqueous}}}{V_{\text{gel}}} \quad (1)$$

where C_{gel} is the concentration of organics in the gel phase; C_{aqueous} is the initial concentration of organics in the aqueous solution or gas phase, a freshly made aqueous solution of toluene (386 ppm) in a large vial (2.6 × 9.0 cm); A_{initial} is the initial UV absorbance of organics in aqueous solution before contact with the gel; A_{final} is the final UV absorbance of organics in aqueous solution after contact with the gel; V_{aqueous} is the volume of the aqueous solution; and V_{gel} is the volume of the gel. We defined the partition coefficient, n , according to eq 2:

$$n = \frac{|\Delta C_{\text{gel}}|}{C_{\text{initial}}} \quad (2)$$

where ΔC_{gel} is the change of the concentration of organics in the gel and C_{initial} is the concentration of organics in the aqueous or gas phase before contact with the gel. We measured the time acquisition spectra of UV absorbance

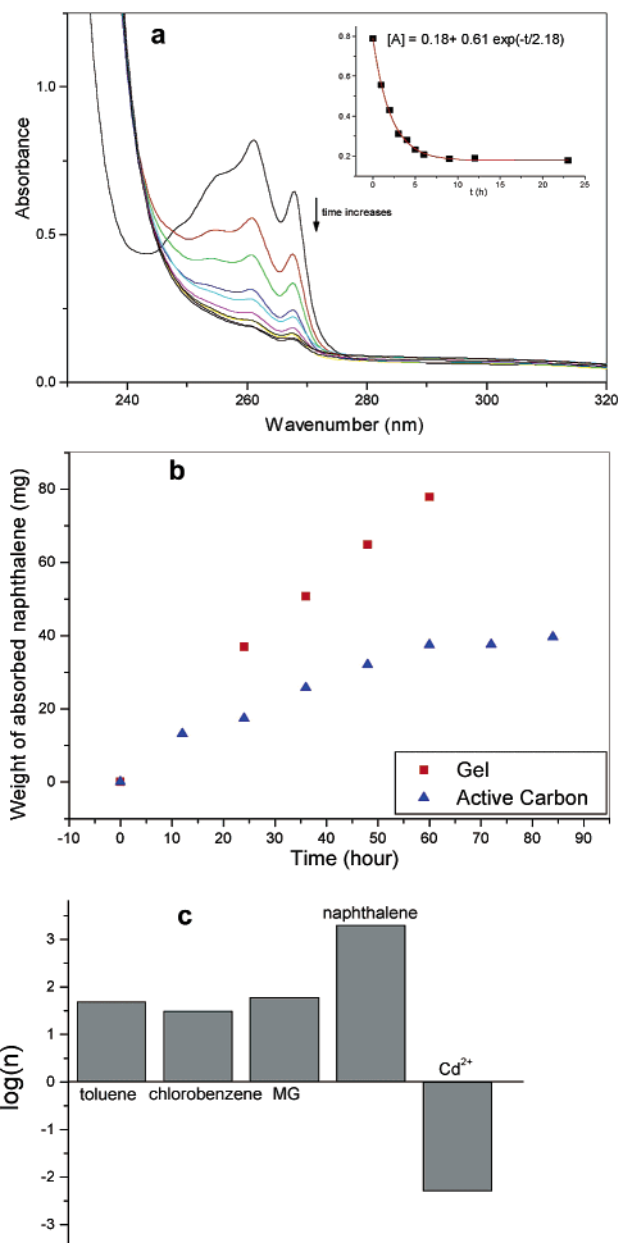


Figure 4. (a) The decrease of UV-vis absorbance of toluene (aq) indicates the extraction of toluene by the metallogel. The inset shows that the decrease of the concentration (squares) follows an exponential decay curve. (b) The weights of naphthalene absorbed by active carbon and the gel from gas phases versus time. (c) The log values of n , versus different substrates, are plotted.

of the toluene solutions until the absorbance stopped decreasing and calculated the concentration of toluene in the gel. We found that the final concentration of toluene in the gel is 18 350 ppm when the initial concentration of toluene in water is 386 ppm, and the calculated n is $\sim 47.0 \pm 2.0$. We applied the same experiment to chlorobenzene and found that the final concentration of chlorobenzene in the gel is 9900 ppm when the initial concentration of chlorobenzene in water is 275 ppm. The calculated n is 36 ± 2.0 . To further prove the gel's ability to enrich ultralow concentrations of organics, we used Malachite Green (MG) instead of toluene and chlorobenzene as the source of organics, because MG has a higher extinction coefficient ($148\,900 \text{ M}^{-1} \text{ cm}^{-1}$ at 616.5 nm) for easier UV detection at part per billion (ppb) levels. Using the same protocol as described before, we observed a rapid decrease of the

concentration of MG in aqueous solution, as shown in Figure 4c, when immersing 0.4 mL of the gel in 40 mL of aqueous solution of MG (660 ppb). The final concentration of MG in the gel is 39.9 ppm after 24 h. The calculated n is ~ 60 . Figure 4c plots the $\log(n)$ versus each chemical.

Enrichment of Organics from the Gas Phase. The gel also enriches organic molecules from the gas phase with an even higher value of n . We placed a vial (2.6×9.0 cm) containing the metallo gel (0.4 mL, 407 mg, and 2% gelator) in a closed chamber (1.5 L) that was constantly saturated with naphthalene vapor (~ 100 ppm). As shown in Figure 4b, after 24 h, the weight of naphthalene absorbed in the gel is 38 mg, corresponding to a concentration of 93 366 ppm in the gel; after 60 h, the total weight of naphthalene absorbed in the gel is 78 mg, corresponding to a concentration of 191 646 ppm in the gel. The partition coefficient, n , is about 1916. For comparison, active carbon (407 mg) was placed in the same chamber along with an equal weight of the gel. As shown in Figure 4b, after 60 h, the total weight of naphthalene absorbed in the gel is about twice that in the active carbon.

Rejection of Ions. The origin of the enrichment of organic molecules stems from the hydrophobicity of the ligands in the coordination polymer networks. The hydrophobicity of the metallo gel, however, prohibits the extraction of the metal ions from aqueous solution. The gel used for metal ion extraction, with the ratio of Pd(en)²⁺/PAC at 1.5, contained free coordination sites (pyridine). We immersed the gel (1.0 mL) in 4.0 mL of Cd(NO₃)₂ aqueous solution (50.00 ppm) and measured the Cd²⁺ and Pd²⁺ concentrations in the aqueous phase by ICP. After 24 h, the concentration of Cd²⁺ in aqueous solution remains at 49.95 ppm, which is less than a 0.11% difference from its original concentration (Figure 4b). We did not detect any Pd²⁺ in the aqueous phase within the detection limits of ICP. These results suggest that the

surface of the gel is hydrophobic despite of the presence of NO₃⁻ on the coordination polymeric networks. The hydrophobicity prohibits the aqueous solution, and thus the metal ions, from penetrating into the gel. This apparent hydrophobicity of the gel was further confirmed when the gel failed to absorb any bovine serum albumin (BSA), essentially a polyanion, after 48 h of immersion in an aqueous solution of BSA (200 ppm).

Conclusion

In conclusion, we have demonstrated a simple and new approach to make a remarkable stable metallo gel, which consists of a coordination polymeric network and an amphiphilic organic solvent (DMSO). This process, using small amount of gelator to control microscopic structures and thus influence the macroscopic behavior, is a useful approach to design and control the properties of materials. Spontaneous enrichment of organic/nonionic molecules at ultralow concentration into the metallo gel, we believe, is a general process and will find useful applications in chemical sensing, catalysis, and separation. This metal–ligand bonding induced gelation may also play a important role in the process of spontaneous assembly of dissolved organic matter into particulate organic matter in the cycling of marine organic matter.²¹ Introducing the unique properties of metals ions into gels will also offer a new opportunity to design novel materials, and the control of each component at the molecular level provides many unexplored opportunities.

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