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A stable metal coordination polymer gel based on a calix[4]arene and its 'uptake' of non-ionic organic molecules from the aqueous phase

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Here we report a coordination polymer based, stable organogel (termed 'metallogel' to emphasize the essential role of metal–ligand bonding during the gelation), which 'uptakes' neutral organic molecules from the aqueous phase.

The uptake of *n*-alkanes, the oxidation substrates of alkylotrophs, is the first and necessary step in the oxidative process in bacteria. By developing specialized cell walls that 'dissolve' and accumulate hydrocarbons and transport them to catalytic sites in their cell membranes, bacteria circumvent the difficulty of enzymatic attack of otherwise low-concentration alkanes in solution.[1] Few systems mimic the uptake processes of alkanes despite their importance. As a first step towards achieving the long-term goal of mimicking the functions of alkylotrophs, we have endeavored to build an artificial system that can uptake trace amounts of non-ionic organic molecules from the aqueous phase. We have built an artificial system from a metal–ligand-bonding enforced organogel[2–5] because (1) unlike most hydrogels, organogels are usually receptive to non-ionic organic molecules; (2) the combination of metal ions and gels allows the integration of the 'uptake' with the catalytic processes; (3) the confinement of metal ions in the gel helps recover catalyst and reduce pollution; and (4) the 'freeze' of metal centers, on the backbone of the network of the gel, may prevent the metal centers from disproportional reactions.

Here we report on the creation of this artificial system, based on a stable organogel (termed 'metallogel' to emphasize the essential role of metal–ligand bonding during the gelation) that 'uptakes' neutral organic molecules from the aqueous phase. This metallogel, virtually 98% of which is dimethyl sulfoxide (DMSO) while still being immiscible with water, exhibits high stability in aqueous solutions over a wide rang of pH (1–13), even at 100 °C, and allows the efficient "uptake" of non-ionic organic molecules. We anticipate that such metallogels will find applications in environmental,[6] catalytic,[7] and separation technologies[8] and that the methodology used to produce the metallogel will provide a simple, easy route to explore and utilize otherwise (mostly) insoluble coordination polymers.

We chose calix[4]arene as the framework to which to attach ligands because of its well-defined and extensively developed chemistry.[9] A calix[4]arene, with multiple binding sites, will promote cross-linking to form a polymeric network that is critical for gelation; the cavity of calix[4]arene can also provide more interstitial space to 'hold' the solvent molecules. Calix[4]arene has served as the gelator in non-polar solvents (cyclohexane, hexane and carbon disulfide),[10] but not as a ligand for making metallogels, at least to our knowledge. In order to maximize the size of the cavities and to introduce the binding sites for metal ions, we synthesized 3-pyridine-azocalix[4]arene (**1**) in 97% isolated yield, using the modified azo-coupling procedure[11] initially reported by Shinkai *et al.*[12]

Compound **1** adapts a cone conformation in the crystal phase[13] and is conformationally flexible in solution. The ^1H NMR spectrum in DMSO-d_6 shows two broad peaks (of geminal protons on the methylene bridge) at 4.30 and 3.65 ppm, which suggests that **1** is conformationally flexible at 25 °C in DMSO. No gelation was observed with **1** alone in solutions (*e.g.*, DMF, DMSO or pyridine). Though the hydrophobicity of the calix[4]arene core makes **1** insoluble in neutral water, **1** dissolves in basic (pH = 13) or acidic (pH = 1) aqueous solutions, probably because of its deprotonatable hydroxyl groups and protonatable pyridine groups.

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We controlled the formation of coordination polymers and metallogels by carefully choosing the metal ions, ligands and solvents. Since $[Pd(en)(H_2O)_2]^{2+}$ (en = ethylenediamine) and pyridine are well known to generate extended molecular structures,[14,15] we used $[Pd(en)(H_2O)_2]^{2+}$ ions to form a coordination polymer and monitored the formation of the polymer and the gel using ^1H NMR in DMSO-d_6. Immediately after adding $[Pd(en)(H_2O)_2](NO_3)_2$ to the DMSO solution of **1**, the peaks of the aromatic protons broadened and the broad peaks of the methylene proton at δ 4.30 and 3.65 disappeared. Nevertheless, the peaks of protons on the ethylenediamine shifted and broadened, indicating the formation of polymers due to coordination. Those peaks became even broader and less intense after the gelation was completed; gelation was confirmed by the inverted test-tube method (Fig. 1). Considering the conformational flexibility of **1** demonstrated by ^1H NMR, we believe that DMSO fills the interstitial space of random conformers of **1** crosslinked by the $Pd(en)^{2+}$ ions (Scheme 1). The typical molar ratios of Pd(II) to **1** are from 1.8 : 1 to 2 : 1, and the percentages of the coordination polymers in the gels are from 0.5 to 2 wt%, corresponding to a molar ratio of the gelator and the solvent of ~ 1 : 10^3. Using $Pd(COD)Cl_2$ as the source of the metal ions, we observed the gelation in DMSO after 72 h,

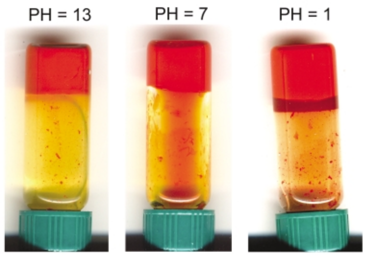
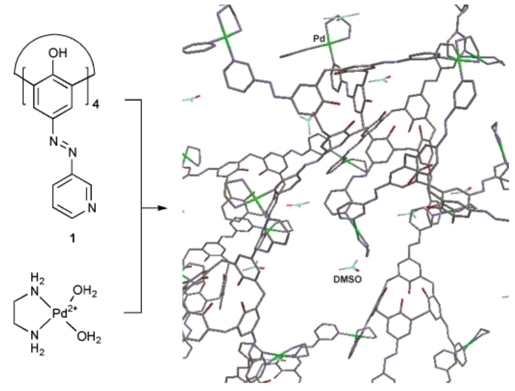


Fig. 1 Images (taken with a flatbed scanner) of the gels at different pH.[16]



Scheme 1 Formation of the possible network of the metallogel.

which was longer than that of $[Pd(en)(H_2O)_2](NO_3)_2$ (typically 4 h) and probably due to a slow ligand-exchange process between COD and pyridine.

The stability of the metallogel depends on the degree of cross-linking. When the ratio of gelator-to-solvent is 0.5 wt%, the formation of the metallogel is thermally reversible. Increasing the ratio of the gelator to 2 wt%, the metallogel cannot be redissolved into DMSO upon heating or ultrasonicating. This result indicates that there is a higher ceiling temperature of the metallogel as the result of more crosslinking at higher concentrations of the gelator. This metallogel is stable (no collapse observed) in most hydrophilic solvents (*e.g.*, THF, DMF, $PhCH_2OH$, CH_3COOH and DMSO) and hydrophobic solvents (*e.g.*, $CHCl_3$, CH_2Cl_2 and toluene), even at elevated temperatures (*e.g.* 110 °C). Although **1** is soluble in an aqueous solution at pH = 13 or pH = 1, the gel, formed by **1** and $[Pd(en)(H_2O)_2](NO_3)_2$ in DMSO, is stable and insoluble in water over a wide range of pH (1–13, Fig. 1), even at 100 °C. Inductively coupled plasma-mass spectrometry (ICP-MS) analysis showed that no Pd^{2+} was leached out of the metallogel. Such stability, exhibited by the metallogel in both hydrophilic and hydrophobic solvents, is uncommon for a gel formed with an amphiphilic solvent such as DMSO. The gel (0.4 ml) completely dissolves in pyridine (2 ml) and collapses and precipitates in acetone (0.8 ml). The precipitated polymers do not act as gelators when added back into DMSO, but instead dissolve in pyridine.

The unique stability of the metallogel allows its efficient "uptake" of non-ionic organic molecules at low concentrations from aqueous phases. We used toluene as the non-ionic organic substrate since it has observable UV absorbance to allow for the easy monitoring at low concentration. We added 40 ml of a freshly made aqueous solution of toluene (570 ppm) into a large vial (2.6 × 9.0 cm) containing 0.4 ml of the gel. We estimated the toluene concentration in the gel† by measuring the time acquisition spectra of UV absorbance of the aqueous solution until the decrease of the absorbance became undetectable. As shown in Fig. 2, the 'uptake' apparently follows first-order kinetics. Such kinetic information suggests that the 'uptake' is most likely physical adsorption in nature. We used the partition coefficient, K,† to define the ability of the 'uptake' by the metallogel. We found that the final concentration of toluene in the metallogel is 18350 ppm when the final concentration of toluene in water is 386 ppm. The calculated value of K is $\sim 47.0 \pm 2.0$, which suggests that $\Delta G_{298} = -2.3 \pm 0.4$ kcal mol^{-1} for the 'uptake' of toluene from water into the metallogel at room temperature. We applied the same experiment to chlorobenzene and found the calculated K to be 36.0 ± 2.0 ($\Delta G_{298} = -2.1 \pm 0.4$ kcal mol^{-1}). The measured K values of the metallogels are comparable with that of the commonly used absorbent, *i.e.*, active carbons, for organics in aqueous solution.

In conclusion, we have demonstrated a simple method to make a novel and stable metallogel, which consists of a coordination polymeric network and an amphiphilic organic solvent. Expansion of coordination polymers from crystalline materials to soft materials—such as gels, will provide a new playground in coordination chemistry to study and utilize other functions of coordination polymers. We are currently investigating the catalytic ability of the metallogel by designing more relevent systems.

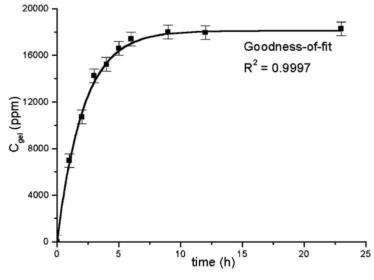


Fig. 2 The concentration increase of toluene (calculated) in the gel *vs.* time.

Notes and references

† We calculated the concentration of toluene in the gel according to:

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

where C_{gel} is the concentration of organics in the gel; $C_{initial}$ is the initial concentration of organics in the aqueous phase; C_{final} is the final concentration of organics in the aqueous phase; $A_{initial}$ is the UV absorbance of organics in the aqueous solution before contacting the gel; A_{final} is the UV absorbance of organics in the aqueous solution after the gel stops 'uptake'; $V_{aqueous}$ is the volume of the aqueous solution; and V_{gel} is the volume of the gel.

We calculated the partition coefficient, K, according to:

$$K = \frac{C_{gel}}{C_{final}} = \left(\frac{A_{initial}}{A_{final}} - 1 \right) \times \frac{V_{aqueous}}{V_{gel}}$$

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