



Cage Compounds

Creating Coordination-Based Cavities in a Multiresponsive Supramolecular Gel

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Abstract: Creating cavities in varying levels, from molecular containers to macroscopic materials of porosity, have long been motivated for biomimetic or practical applications. Herein, we report an assembly approach to multiresponsive supramolecular gels by integrating photochromic metal–organic cages as predefined building units into the supramolecular gel skeleton, providing a new approach to create cavities in gels. Formation of discrete O-Pd₂L₄ cages is driven by coordination between Pd²⁺ and a photochromic dithie-nylethene bispyridine ligand (O-PyFDTE). In the presence of suitable solvents (DMSO or MeCN/DMSO), the O-Pd₂L₄ cage molecules aggregate to form nanoparticles, which are fur-

ther interconnected through supramolecular interactions to form a three-dimensional (3D) gel matrix to trap a large amount of solvent molecules. Light-induced phase and structural transformations readily occur owing to the reversible photochromic open-ring/closed-ring isomeric conversion of the cage units upon UV/visible light radiation. Furthermore, such Pd_2L_4 cage-based gels show multiple reversible gel–solution transitions when thermal-, photo-, or mechanical stimuli are applied. Such supramolecular gels consisting of porous molecules may be developed as a new type of porous materials with different features from porous solids.

Introduction

Supramolecular gels are a kind of stimulus-responsive soft material that can undergo smart changes in response to external stimuli,^[1] thereby showing potential applications in materials science,^[2] drug delivery,^[3] and construction of supramolecular nanostructures.^[4] They are usually assembled from low-molecular-mass organogelators based on a "bottom-up" approach through synergistic effect of various noncovalent interactions, such as hydrogen bonding, π - π stacking, metal-organic coordination, hydrophobic interactions, and van der Waals forces.^[5] These weak and therefore reversible interactions make supramolecular gels responsive and readily tunable by mechanical, thermal, and chemical stimuli, such as temperature, light, pH, and ultrasound. Nevertheless, some uncertainty of the gel structure is present. For example, the solid-like gel skeleton is known to be amorphous in nature and the network porosity is hard to control and define.^[6]

As a way to tune the gel structure and porosity more definitely, endowing supramolecular gelators with predefined cavities is expected to be able to open up a new application gate to gel materials, for example, incorporating host–guest chemistry of cavitands into the gel systems.^[7] However, this promising field combining interface of supramolecular gel and host– guest chemistry is still in its infancy, and endeavors devoted to creation of such gel materials are only limited to a few cavitycontaining gelators, for example, covalent host molecules like

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cyclodextrin, curcurbituril, calixarene and macrocycles, and coordination complexes of metallocyclic and grid structures.^[7–9] On the other hand, by incorporating active moieties into molecular gelators, functional supramolecular gels can be fabricated with modulated properties.^[10] For example, light-induced reversible gelation can be achieved by introducing photoactive/photochromic moieties like azobenzene^[11] or dithienyle-



Figure 1. Schematic representation of gelation process from $O-Pd_2L_4$ cage molecules to hierarchically porous supramolecular gels showing reversible gel-to-solution transformations under external stimuli.

thene chromophores^[12] into gelators.^[13] Considering the above background, we herein report a new synthetic approach to supramolecular gels by using photoactive metal–organic cages (MOCs) as gelators. The resulting supramolecular gels contain Pd_2L_4 coordination cages with predefined internal cavities, offering hierarchical porosity of mesopores and nanocages, as well as multiresponsive properties as shown in Figure 1.

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Results and Discussion

Design approach

The design of supramolecular gels consisting of porous molecules^[14, 15] may provide a new type of porous material with different features from known porous solids. For the crystal engineering of porous solids, the design and assembly of zeolitelike porous metal–organic frameworks (MOFs) by using discrete MOCs or coordination polyhedra as supramolecular building blocks (SBBs) has been well-established (Figure 2a).^[16]



O Porous molecules **E** Supramolecular interactions

Figure 2. Schematic representations of a) porous solids and b) cavity-containing gels.

In contrast, supramolecular gels undergo readily gel-to-solution phase transitions when external stimuli are applied. Additionally, such gels are in a unique phase that, by weight and volume, they are mostly liquid, yet they behave like a solid due to the existence of 3D cross-linked networks within the liquid (Figure 2 b).^[17]

The formation of a gel matrix often demands collaborative interplaying of multiple intermolecular interactions,^[6,17] which is in contrast to cage-containing MOFs that are usually assembled from periodic growth of cage SBBs in a well-ordered fashion through directional metal-ligand coordination.^[18] It is known that the aggregation of cage SBBs in solution can create fascinating superstructures like vesicles and micelles,^[19] however, incorporation of cage SBBs into gel networks still waits for exploration. As exemplified in Figure 1, the first step is to assemble the Pd₂L₄ coordination cages with an internal cavity as supramolecular gelators. Secondly, these cage precursors aggregate in the presence of suitable solvents (here DMSO or MeCN/DMSO) to form nanoparticles. Finally, once the nanoparticles further aggregate in a cross-linked and disordered fashion rather than periodic crystallization, formation of gel matrix is possible when sufficient and appropriate intermolecular interactions are available for gelation (Figure 1).^[6] Such a supramolecular gel may bring in versatile host-guest chemistry of nanoscaled coordination cages, since they have been proven to be able to selectively encapsulate quest molecules or ions and modify the reactivity of guest species,^[20] thus showing potential applications in catalysis,^[21] sensors,^[22] and controlled release.^[23,24] Specifically, many analogous Pd_2L_4 coordination cages have already been reported to show interesting guest-binding ability within its cavity^[23] or light-triggered guest encapsulation.^[24]

Gelation studies

It is well known that the dithienylethene chromophore can undergo open-ring to closed-ring isomerization by irradiation with UV light, and the reversal by visible-light irradiation. Additionally, diarylethenes represent most promising switch units because of their unique fatigue resistance and thermal irreversibility.^[25] Therefore, a bipyridine-type ligand with diarylethene(dithienylcyclopentene) moiety as spacer, PyFDTE, was synthesized (Scheme 1, see the Supporting Information for experi-



Scheme 1. Chemical structures of O-PyFDTE and O-PyDTE.

mental details) for the gelation test. The open-ring isomer O-PyFDTE (O-Form; light-brown color) can be transformed to the closed-ring isomer C-PyFDTE (C-Form; deep-blue color) upon UV irradiation, and its reverse process occurs photochemically upon visible light, readily identifiable by chemical shifts in the ¹H NMR spectra and photochromism in the UV/Vis spectra (Figure 3 and the Supporting Information, Figures S1 and S2).

Both the isomers, O-PyFDTE and C-PyFDTE, were tested for their gelation behaviors with various metal salts, including $[Pd(NO_3)_2]$, $[Ni(NO_3)_2] \cdot 6 H_2O$, $[Cu(NO_3)_2] \cdot 3 H_2O$, $[Zn(NO_3)_2] \cdot 6 H_2O$, $[Cd(NO_3)_2] \cdot 4 H_2O$ and $[Co(NO_3)_2] \cdot 6 H_2O$. Only $[Pd(NO_3)_2]$ was found to be able to induce gelation with O-PyFDTE, which can



Figure 3. Gelation routes of CCG-1 from photochemically reversible O- and C-forms of PyFDTE, and its versatile responsiveness towards light-, thermo-, mechano-, and anion-stimuli, showing reversible or irreversible gel-to-solution transitions as well as color changes.

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be simply checked by the inversion test. Meanwhile, gelation was found to occur in DMSO among various pure organic solvents tested (DMSO, DMF, DMA, CH₃CN, 1,4-dioxane, THF, see the Supporting Information, Table S1). Gels could also be obtained in MeCN/DMSO solvent mixtures (v/v < 1:1). It is noticeable that no gelation was observed for the closed-ring C-PyFDTE with any tested metal salts and solvents (C-PyFDTE solution was obtained by exposing an O-PyFDTE solution to UV light with transformation of O-Form to C-Form > 95 %). Transparent gels could be obtained in DMSO when the Pd/O-PyFDTE ratio varied from 1:2 to 1:1 (the Supporting Information, Table S2). Additionally, gelation could be observed under an O-PyFDTE concentration as low as 0.025 mol L⁻¹ (the Supporting Information, Table S3). As a representative, the gel of Pd/O-PyFDTE = 1:2 system (c_L = 0.025 mol L⁻¹) was investigated in detail (denoted as coordination cage-based gel-1, CCG-1). In general, CCG-1 was obtained through two routes shown in Figure 3: 1) Assembly of Pd²⁺ and O-PyFDTE in 1:2 ratio gives rise to homogeneous solution of O-Pd₂L₄ cages, which undergoes gelation for about 10 h at room temperature to lead to CCG-1; 2) Assembly of Pd²⁺ and C-PyFDTE in 1:2 ratio in the dark gives rise to deep-blue solution of C-Pd₂L₄ cages, which cannot undergo gelation in the dark, but undergoes gelation readily when exposed in visible light for about 10 h at room temperature, offering CCG-1 as in route A. For comparison, ligand PyDTE cannot gelate any tested metal salts under similar conditions (see below).

The gel **CCG-1** is thermo-reversible (Figure 3). Upon heating, a gel-to-solution transition was observed, and the solution reverted to the gel by cooling to room temperature. The gel-to-solution transition temperature (T_{gel}) elevated considerably with increasing gelator concentration (the Supporting Information, Figure S3). Specifically, T_{gel} increased from 70 to 90 °C as the gelator concentration increased from 0.025 to 0.10 mol L⁻¹. Additionally, the solution mixture with lower concentration took a much longer time for gelation. For example, the gelation of a 0.025 mol L⁻¹ solution took about 10 h, whereas a solution of 0.10 mol L⁻¹ only took 2 min. When the concentration was above 0.06 mol L⁻¹, the gelation occurred fast (\leq 10 min) (the Supporting Information, Figure S3).

The morphology of gel **CCG-1** was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Figure 4). The 3D gel network was aggregated from nanoparticles of about 20–50 nm size. The gel skeleton composed of nanoparticles is amorphous in the wet gel and xerogel states, evidenced by the broad and featureless diffraction peaks of powder X-ray diffraction (the Supporting Information,



Figure 4. a) SEM and b) TEM images of gel CCG-1 (the bars represent 1.0 and 0.1 μ m from left to right, respectively).

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Figure S4). Energy dispersive X-ray spectroscopy disclosed the presence of N, F, S and Pd elements in the gel (the Supporting Information, Figure S5). Fourier transform infrared spectra of the xerogel unveiled the presence of PyFDTE ligand in the metal coordination sphere (the Supporting Information, Figure S6). The strong absorption band at 1383 cm⁻¹ is assignable to the NO₃⁻ vibration. The surface analysis by X-ray photoelectron spectroscopy showed a signal at 338.2 eV in the Pd 3d_{5/2} region, confirming the coordination of Pd^{II} to PyFDTE (the Supporting Information, Figure S7).

¹H NMR and ESI time-of-flight mass spectroscopic studies evidently verified that the gel particles are composed of $[Pd_2(O-PyFDTE)_4]$ cage molecules. ¹H NMR titration was performed in $[D_3]MeCN/[D_6]DMSO$ solvent mixture (v/v=2:1) in which no gelation occurred (Figure 5). Upon proportional addi-



Figure 5. ¹H NMR titration of O-PyFDTE with $[Pd(NO_3)_2]$ in $[D_3]MeCN/$ $[D_6]DMSO$ solvent mixture (v/v=2:1). Only aromatic proton signals are shown.

tion of Pd²⁺ into the solution of O-PyFDTE, the spectral profile of the pure ligand showed drastic changes. New proton signals appeared along with relatively decrease of the ligand signals. When the metal-to-ligand ratio reached to 1:2, the NMR spectrum turned into one set of new signals, corresponding to resonance patterns of pure ligand with all chemical shifts of the ligand protons shifted remarkably downfield, indicating that complexation had occurred between O-PyFDTE and Pd²⁺ to lead to the assembly of [Pd2(O-PyFDTE)4] cages.^[26] The protons H_b and H_e on the pyridine ring in the neighboring positions of N donor showed much more significant downfield shifts in comparison with other protons, clearly confirming the coordination through Pd-N bonding due to the electron-withdrawing effect by the Pd²⁺ ion. No further resonance changes happened when Pd/PyFDTE ratios were increased from 1:2 up to 2:2, suggesting that the Pd/L = 1:2 cages are the most thermodynamically preferred solution species. Furthermore, high-resolution ESI-MS spectra of a dilute dispersion of the gel in MeCN showed salient peaks at m/z 788.0231 and 1213.0285 (the Supporting Information, Figure S8), exactly corresponding to the species $[Pd_2L_4 + NO_3]^{3+}$ and $[Pd_2L_4 + 2NO_3]^{2+}$, respectively, verified by closely matched isotopic distribution simulations. No other obvious coordination species of higher molecular mass



were observed. These spectroscopic results and solution coordination behaviors may support the formation of Pd_2L_4 cage molecules and the integration of the cage molecules into the gel skeleton.

In addition, the gelation dependence on the L/Pd ratios is actually controlled by assembly of Pd₂L₄ cage precursors as revealed by the NMR titration study (Figure 5). When L/Pd ratio was 2:1, quantitative Pd₂L₄ cages were obtained in MeCN/ DMSO solution. Excess Pd²⁺ ions (e.g., L/Pd=2:2) did not affect the solution structure. However, when excess ligand was present (e.g., L/Pd = 2:0.67), Pd_2L_4 cage molecules showed remarkable dynamic behavior as evidenced by the broadened and complicated signals. Such solution assembly behaviors of Pd₂L₄ cage showed profound influence of the gelation. Only when all O-PyFDTE ligands were used up for formation of Pd_2L_4 cages, that is, L/Pd = 1:1 and 2:1, did the gelation occur (the Supporting Information, Table S2). When the ligand was in excess, that is, L/Pd=4:1, no gelation occurred. In addition, it should be noted that the presence of too many excess Pd²⁺ ions, for example, L/Pd = 1:2, also prevented the gelation process (the Supporting Information, Table S2).

Light-triggered structural and gel-to-solution transitions

The Pd_2L_4 solution underwent reversible photochromism in the solution state upon irradiation with UV and visible light arising from ring-closing/opening reactions as expected for dithienyle-thene derivatives (Figure 6). Such structural interconversion be-



Figure 6. Interconversion between open-ring $O-Pd_2L_4$ and closed-ring $C-Pd_2L_4$ isomers in solution at 343 K and a) Pd/C-PyFDTE = 1:2 solution (C- Pd_2L_4) kept in the dark ($c_L = 0.025 \text{ mol } L^{-1}$); b) under visible light for 1 min (C- Pd_2L_4 and $O-Pd_2L_4$ mixture); c) under visible light for 30 min ($O-Pd_2L_4$). Only aromatic proton signals are shown.

tween open-ring O-Pd₂L₄ and closed-ring C-Pd₂L₄ isomers can be further monitored by in situ UV/Vis spectra. The major absorption band of the Pd/L=1:2 dilute solution in the open form O-Pd₂L₄ was found at about 290 nm, which is ascribed to π - π * transition (Figure 7). Irradiation of the solution with 254 nm UV light led to appearance of new absorptions band at about 385 and 595 nm, which are attributed to the increased π -electron delocalization in the closed isomer C-Pd₂L₄. The isosbestic points are centered at 257 and 320 nm, suggesting that only two absorbing species, namely O-Pd₂L₄ and C-Pd₂L₄ isomers, are involved in light-triggered structural interconversion.



Figure 7. Absorption spectra of the Pd/O-PyFDTE = 1:2 solution ($c_L = 1.0 \times 10^{-4} \text{ mol L}^{-1}$ in DMSO) under 254 nm UV light irradiation, showing O-Pd₂L₄ to C-Pd₂L₄ structural conversion.

Formation of the closed-ring C-Pd₂L₄ cage structure in the above process was evidenced by ESI-MS and NMR spectroscopic examination. The high-resolution ESI mass spectra of the C-Pd₂L₄ solution showed a clear sequence of peaks for $[Pd_{2}L_{4}]^{4+}$, $[Pd_{2}L_{4} + NO_{3}^{-}]^{3+}$, and $[Pd_{2}L_{4} + 2NO_{3}^{-}]^{2+}$ species corresponding to sequential loss of nitrate anions from the intact mother coordination cage [Pd₂L₄](NO₃)₄ (the Supporting Information, Figure S9). This spectral observation closely resembles the ESI-MS result of $O-Pd_2L_4$ cage mentioned above, because the O-Pd₂L₄ and C-Pd₂L₄ isomers have exactly the same molecular weight. However, the structural interconversion between these two isomers can be easily identified by the in situ ¹H NMR monitoring (Figure 6). The initial and completely converted Pd₂L₄ cage species show well-recognized resonance patterns corresponding to respective isomers (the Supporting Information, Figure S10), whereas the incompletely converted intermediate shows a mixture of two isomers.

Light-induced structural conversion between the C-Pd₂L₄ and O-Pd₂L₄ isomers readily leads to a gel-to-solution transition (Figure 1) because the C-Pd₂L₄ isomer cannot form a gel at room temperature but the O-Pd₂L₄ isomer can. The transition from the brown gel state (**CCG-1**) to the blue solution state (C-Pd₂L₄) was induced by 254 nm UV irradiation for 12 h. The resultant low viscosity solution was stable at room temperature when kept in dark, but the blue solution faded upon exposure to visible light for 20 min and turned to a gel again after 10 h. The gel-to-solution transition was fully reversible and repeatable for many times. Further investigations revealed that 15% percentage conversion of the open-ring to closed-ring isomer was enough to break down the gel. In other words, the critical conversion percentage of C-Pd₂L₄ cages is below 15% (determined on the basis of the NMR spectral change).

Gelation mechanism

The above results reveal that formation of $O-Pd_2L_4$ cage precursors is essential in the gelation of **CCG-1**. The formation of the Pd_2L_4 cage structure was further confirmed by two-dimensional diffusion-ordered spectroscopy (DOSY) ¹H NMR. DOSY ¹H NMR

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spectroscopy was utilized to measure the diffusion coefficients of the solution species assembled from the Pd/O-PyFDTE = 1:2 solution in [D₃]MeCN/[D₆]DMSO (v/v=2:1) (the Supporting Information, Figure S11). The self-diffusion coefficient D for the cage was determined to be $4.47 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ at 298 K. According to the Stokes-Einstein Equation, the approximate hydrodynamic radius is calculated to be 9.21 Å for the solution species. The radius is in agreement with formation of the Pd₂L₄ cage structure. In addition, the Pd_2L_4 cage complex precipitated by diffusion of hexane into the MeCN/DMSO solution was found to gelate DMSO again.

To understand the role of Pd₂L₄ cage molecules in the gelation, variable-temperature ¹H NMR spectroscopy was investigated within a temperature range 300-353 K for both O-Pd₂L₄ and C-Pd₂L₄ isomers, which show distinguishable gel and solution states (the Supporting Information, Figure S12). At room temperature, no salient resonance signals of O-Pd₂L₄ cages were observed in the gel state, suggesting all the cage molecules are fixed as part of the gel network. Upon heating the O-Pd₂L₄ gel system, a gradual improvement of the signal resolution was observed. Such increase of cage gelator signals upon heating is due to the enhancement of molecular mobility and dissociation of the gel network.^[11d, 31] Above the gel-to-solution transition temperature (343 K), well-resolved signals of the Pd₂L₄ cage species were observed. The reverse cooling process afforded the opposite observations. This suggests that the O-Pd₂L₄ cage species aggregate gradually and finally form the gel as the temperature decreases. In contrast, the C-Pd₂L₄ isomer system persists in the solution state in the testing temperature range. When measured in the dark at room temperature, the spectrum showed broadened but salient proton signals, indicating slowdown of the $C-Pd_2L_4$ cage dynamics in solution but no gelation. As expected, the proton resonances became wellresolved with an increase in temperature.

To obtain more gel structural information, the O-Pd₂L₄ system was investigated in [D₃]MeCN/[D₆]DMSO solvent mixtures by ¹H NMR spectroscopy. As mentioned above, gelation also occurs in MeCN/DMSO solvent mixtures (v/v < 1:1) but sensitively depends on the MeCN/DMSO ratio. When the content of MeCN in MeCN/DMSO mixture increases, the system transforms from gel (v/v \leq 1:1) to solution (v/v > 1:1) (the Supporting Information, Figure S13). Interestingly the signals of O- Pd_2L_4 cage were observed for the gels as seen for the solutions (Figure 8). The broadened signals turn sharp gradually as the MeCN content increases, revealing that the O-Pd₂L₄ cages integrated in the gel network become loose and more dynamic even if the overall gel state was retained. This observation is comprehensible because intermolecular interactions are less favored in less polar MeCN than in DMSO, thus allowing faster exchange between discrete cage molecules and those integrated in the gel network.^[27] In addition, when the gel (v/v = 1:3) was heated, the resonances became well resolved (the Supporting Information, Figure S14). These results from ¹H NMR spectroscopy show that the O-Pd₂L₄ cage molecules dissociate gradually from the gel matrix as the temperature increases or as the MeCN content increases at room temperature; in other words, O-Pd₂L₄ cage molecules are gradually incorporated in



Figure 8. ¹H NMR spectra of O-PyFDTE/[Pd(NO₃)₂] = 2:1 in [D₃]MeCN/ [D₆]DMSO solvent mixtures (v/v = 1:19, 1:7, 1:3, 1:1, 5:3, 2:1) $(c_1 = 0.025 \text{ mol L}^{-1})$ at room temperature. Only the signals of aromatic protons are shown. Prior to analysis, the reaction mixtures were allowed to stand overnight. The v/v = 1:19, 1:7, 1:3, 1:1 systems formed gels and the v/ v=5:3, 2:1 systems were solutions.

the gel matrix as the temperature decreases or as the MeCN content decreases. This suggests that the gel matrix is mainly constituted by $O-Pd_2L_4$ cage molecules and the solvent plays an important role in the gelation process as well.

To reveal the role of counteranions, $[Pd(CH_3CN)_4(BF_4)_2]$ instead of $[Pd(NO_3)_2]$ was used as the Pd^{2+} source to treat with O-PyFDTE. Gelation occurred too when NO₃⁻ was replaced by BF₄⁻ (the Supporting Information, Figure S15). ¹H NMR spectroscopy revealed the formation of O-Pd₂L₄ cage species in solution. It suggests that both weakly coordinating NO₃⁻ and BF_4^- anions are able to assist Pd_2L_4 cage formation and therefore gelation. However, the coordinative anions exhibited rather different behaviors, such as CI^- , Br^- , I^- , and AcO^- , which significantly disturbed gelation process and exhibited anion responsiveness.

The anion responsiveness study was performed by the following method: Tetrabutylammonium (TBA) salts with different counteranions, TBA-CI, TBA-Br, TBA-I, TBA-BF₄, and TBA-OAc in 50 μ L of DMSO (molar ratio of anion/L=2:1), were layered on top of the vials containing the gel CCG-1 (0.2 mL). After the vials were left standing at room temperature, the gels diffused with Cl⁻, Br⁻, l⁻, and AcO⁻ were all converted into solutions within a few hours, whereas the gel with BF₄⁻ remained intact (the Supporting Information, Figure S16). ¹H NMR spectroscopic analysis of the resultant solution after diffusion with the coordinating anions, showing the proton signals of free ligand and confirming dissociation of Pd₂L₄ cages. The results show that the coordinating anions (Cl⁻, Br⁻, l⁻, and AcO⁻) may compete with the Pd-N binding interactions within the O-Pd₂L₄ cage, thus causing dissociation of the cage building units thereof destroying the gel matrix. In contrast, the non-coordinating anion (BF₄⁻) has little effect on the gelation state. Therefore, the coordinating anions are able to trigger gel-to-solution transformation (Figure 1).^[28]

To explore whether fluorine atoms on PyFDTE ligand play a role in gelation, a structurally related ligand was prepared for comparison, namely PyDTE (Scheme 1). PyDTE is an analogue of PyFDTE without substituted fluorine atoms on the DTE

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moiety. PyDTE undergoes similar open-ring to closed-ring isomeric transformation and assembles similar Pd_2L_4 cages in solution. Unexpectedly, gelation did not occur for a Pd/PyDTE = 1:2 mixture in DMSO under similar conditions. Instead, a viscous solution was obtained. This observation implies that the fluorine atoms may take part in the aggregation of Pd_2L_4 precursors and subsequent gelation, presumably through fluorine-involved weak intermolecular interactions.^[29]

To understand why gelation only occurs to the open-ring O-Pd₂L₄ isomer rather than the closed-ring C-Pd₂L₄ isomer, structural simulation has been carried out for both the isomers (see the Supporting Information). The C-Pd₂L₄ cage displays a much more rigid conformation and regular shape, whereas the O-Pd₂L₄ cage permits flexibility and geometric freedom to its component ligands and substituting groups (the Supporting Information, Figures S17 and S18). Moreover, the S atoms in the dithienylethene moieties are oriented outwards in between every two ligands in O-Pd₂L₄ cage structure, but completely restrained inwards into the cage cavities in C-Pd₂L₄ isomer. Instead, only hydrophobic methyl groups are positioned in the vacant space between the ligands. These distinct structural geometry and conformation may impart different intermolecular interacting environment to O-Pd₂L₄ and C-Pd₂L₄ isomers, thus causing different interactions between the cage molecules as well as interactions with surrounding anions and solvent molecules. O-Pd₂L₄ cage isomers may provide more chances to form intermolecular interactions with adjacent species, facilitating gelation process, which indeed needs synergistic interplays from multiple intermolecular weak forces.

The aggregation process of O-Pd₂L₄ cage molecules into larger nanoparticles was estimated by a dynamic light scattering (DLS) study (Figure 9). In the freshly prepared O-Pd₂L₄ solution (c_L =0.025 mol L⁻¹), around 24 nm particles were recorded to show the initial aggregation of O-Pd₂L₄ molecules to nanoparticles. Electrostatic attraction mediated by counterions may be one of important forces inducing the initial aggregation.^[19,30] The Pd₂L₄ cage unit carries four positive charges, thus attracting counteranions to surround the cage species by electrostatic forces. Sharing of the anionic sphere among the multivalent cage species may hold them together to form larger nanoparticles.^[31] In the meantime, the O-Pd₂L₄ cage contains



Figure 9. DLS particle size as function of reaction time for the Pd/O-PyFDTE=1:2 reaction system in DMSO (c_L =0.025 mol L⁻¹) at room temperature.

four O-PyFDTE ligands in an unrestricted conformation, exposing S atoms, F substituents, and aromatic organic moieties to the outer sphere, facilitating formation of multiple intermolecular interactions probably involving these heteroatoms, DMSO solvent molecules, NO₃⁻ anions, as well as hydrophobic interactions and $\pi \cdots \pi$ stacking interactions. The evidence of $\pi \cdots \pi$ stacking interactions can be testified from UV/Vis spectra of the O-Pd₂L₄ cage solutions, which indicate that the adsorption maximum shows significantly redshifted from 286 to 304 nm as the concentration increased from 1.0×10^{-6} to $1.0 \times$ 10⁻⁴ mol L⁻¹ (the Supporting Information, Figure S19). Formation of these intermolecular interactions may be able to stabilize the initially aggregated nanoparticles, and to further induce them to grow gradually. The nanoparticles continue to grow to \approx 150–170 nm after 6 h, and then fell beyond the testing scope of DLS instrument (Figure 9). This is consistent with the above SEM and TEM study. In comparison, different aggregation was observed for the solids obtained from the C-Pd₂L₄ cage solution in DMSO (the Supporting Information, Figure S20) and the $O-Pd_2L_4$ cage solution in MeCN/DMSO (the Supporting Information, Figure S21). During this period of time, the aggregated nanoparticles may form an open network to trap solvent molecules, finally yielding the gel CCG-1. Therefore, the gelation process should start from assembly of the O-Pd₂L₄ cage molecules, proceeding through formation of nanoparticle dispersion, and subsequent aggregation into monolithic networks (Figure 1).^[32]

However, it is worth mentioning that gelation is a complicated behavior subject to subtle influence of various intermolecular interactions including solvent–gelator interactions. The exact gelation mechanism is hard to fully understand because we cannot directly determine the molecular structure of the gel matrix according to the present techniques. Therefore, the gel structural information mainly comes from dissociated species in the liquid phase. Since coordination oligomers/polymers are well known to assist gelation,^[6] we cannot exclusively rule out the presence of trace amounts of coordination oligomer/ polymer species in the O-Pd₂L₄ gel; however, our experimental results indicate that the gel skeleton is mainly based on O-Pd₂L₄ cage species and the contribution of possible polymeric species is definitely beyond the NMR detection.

Thixotropic and rheological studies

The gel **CCG-1** exhibits thixotropic response to external large straining. It transformed into a free-flowing viscous liquid by shaking the vial for 2–3 min, and the resulting free-flowing liquid reverted back to the gel after resting for about 10 h (Figure 3). This process was monitored by ¹H NMR spectroscopy (the Supporting Information, Figure S22). In the gel state no salient proton signals were observed, however, some broad signals of O-Pd₂L₄ cages appeared after shaking. These signals observed after shaking are similar to those before gelation. This suggests that the cage molecules may escape from the gel matrix and turn "free" to some degree upon shaking.

The thixotropism or mechano-responsive behavior of the gel **CCG-1** was investigated in detail by rheological techniques.

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Figure 10. Rheological tests of gel CCG-1: a) strain sweep; b) frequency sweep; c) time sweep; d) three cycles of deformation and recovery processes.

Firstly, the gel was monitored as functions of shear strain and dynamic frequency at room temperature to determine the linear viscoelastic regime (Figure 10a, b). At a low strain the storage modulus G' (ca., 69 Pa) was more than one order of magnitude greater than the loss modulus G'' (ca., 6 Pa), indicating dominant elastic characters of the gel. The moduli are lower than those of normal low molecular-mass gels.^[33] Below the strain of 5% as the upper limit of the linear viscoelastic regime, the energy storage modulus and loss modulus kept constant. With the strain increases gradually, the energy storage modulus G' fell sharply, whereas the loss modulus firstly increased and then fell, indicating that the gel began to breakup partially. At a critical value of 130% strain, the storage modulus G' was equal to the loss modulus G''. Above the critical value of 130% strain, the loss modulus G'' became greater than the storage modulus G', which indicated that the network of the gel was completely destroyed. It is clear that the values of G'are always greater than those of the corresponding G'' within the frequency range 0.1–100 rad s⁻¹. Below the frequency limit of 100 rad s⁻¹, both moduli exhibited weak dependence on frequency change, indicating typical viscoelastic behavior. Remarkably, when the large strain was removed, the gel recovered immediately (G' > G'') under 2% strain and 6.283 rad s⁻¹ by monitoring the time evolution of G' and G'' (Figure 10c). This confirms that the gel features a thixotropic behavior, which is a key property for real-life applications of gel-based materials.[34]

To further confirm the gel thixotropic property, a typical thixotropy loop test was performed (Figure 10 d). When a large strain (500%) was applied for 10 s, the gel was completely destroyed (G'' > G'). Once the high strain was canceled, the elasticity recovered immediately after 20 s (G' > G''). Such a thixotropy test can be repeated three times at least. This recovery time is comparable with that of low-molecular-mass organogels^[35] and shorter than that of metallogels.^[36]

Thixotropic behavior has been previously studied for lowmolecular-mass gels.^[35,37] The present study unveils that the gels composed of cage molecules can afford similar thixotropic property. Interestingly, the present gels have a different nano-particle-based morphology. The mechano-responsive behavior may be related to the electrostatic interactions and other weak intermolecular interactions between $O-Pd_2L_4$ cage building units, which are characteristic of non-directional and self-corrective forces.

Conclusion

A multiple stimuli-responsive metal-organic gel (CCG-1) has been obtained on the basis of Pd₂L₄ coordination cage assembly utilizing a dithienylethene-derivatized photochromic bispyridine ligand. The gelation process involves firstly the formation of Pd_2L_4 cage molecules from Pd^{2+} salts and the openring dithienylethenebispyridine isomer O-PyFDTE. Then the O-Pd₂L₄ cage molecules aggregate in DMSO to form nanoscaled particles, which are further cross-linked to generate 3D gel matrix with the aid of multiple supramolecular interactions. The presence of O-Pd₂L₄ cage building units was evidenced by ¹H NMR and DOSY ¹H NMR spectroscopies and ESI-MS. Control experiments and structural simulation show that the open-ring conformation and the fluorine substituents are important for the intermolecular interactions and final gelation. The gel CCG-1 is anion-responsive towards coordinative anions because the addition of coordinative anions to the gel system dissociates the Pd₂L₄ cages, thus resulting in collapse of the gelatinous state to a solution. Remarkably, the viscoelastic gel CCG-1 exhibits reversible multistimuli-responsive behaviors by exposure to external temperature, light, and shear stress, showing various stimulus-triggered gel-to-solution interconversions with the overall Pd₂L₄ cage topology well kept. Among these phase interconversions, the gel-to-solution transition controlled by UV/visible light irradiation is accompanied with the structural transformations between the ring-open O-Pd₂L₄ and the ringclosed C-Pd₂L₄ cage isomers. Nevertheless, the O-Pd₂L₄ cage molecules are kept intact in temperature- or shear-stress-regulated gel-to-solution transitions. The present study suggests that coordination cages of predefined shape/size and inner cavity can be used intelligently as promising building blocks for creation of responsive and smart soft materials. In this way, versatile host-guest chemistry can be introduced into gel materials. It also suggests that supramolecular gels consisting of porous molecules may be developed as a new type of porous materials because they are mostly liquid, yet they behave like a solid and they undergo readily gel-to-solution transitions.

Experimental Section

Materials and general methods

All starting materials and solvents were obtained from commercial sources and used without further purification unless otherwise indicated. 3-Bromo-2-methyl-5-(3-pyridyl)thiophene^[38] and O-PyDTE^[39] were synthesized according to the published methods. The powder X-ray diffraction was recorded on a Bruker D8 Advance diffractometer at 40 kV, 40 mA with a Cu target tube and a graphite monochromator. Infrared spectra were measured on

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a Nicolet Avatrar 330 FT-IR spectrometer with KBr pellets. ¹H NMR spectra were recorded on AVANCE III 400 MHz Spectrometer. UV/ Vis absorption spectra were recorded using a Shimadzu/UV-250PC spectrophotometer. The UV irradiation studies were carried out using standard hand-held lamps (254 and 365 nm) used for visualizing TLC plates (WFH-12B), and the visible-light irradiation studies were carried out by using a 150 W halogen source (Philips 13629 EKE) that was passed through a Y48(>450) cutoff filter to eliminate higher energy light.

Synthesis of O-PyFDTE

The synthetic route for PyFDTE is shown in Scheme S1 (the Supporting Information). A nBuLi/hexane solution (3.1 mL, 1.6 mol L⁻¹, 5 mmol) was added dropwise at -78 °C under N₂ atmosphere to a solution of 3-bromo-2-methyl-5-(3-pyridyl)thiophene (1.26 g, 5 mmol) in anhydrous THF (50 mL). After 30 min, octafluorocyclopenene (0.34 mL, 5 mmol) was slowly added and the reaction mixture was stirred for 1 h at -78 °C. The reaction mixture was allowed to slowly warm to the room temperature and guenched by diluted hydrochloric acid. The mixture was extracted with diethyl ether and the ethereal extract was dried with anhydrous MgSO₄ and evaporated to dryness. The crude solid product was purified by column chromatography on silica gel using petroleum ether/ ethyl acetate (v/v = 1:1) as the eluent to give a yellowish green solid (0.45 g, 34%). ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): $\delta =$ 8.87 (s, J=1.9 Hz, 2 H), 8.53 (d, J=4.8, 2 H), 8.05 (dd, J=8.0, 2.3 Hz, 2H), 7.66 (s, 2H), 7.46 (dd, J=8.0, 4.8 Hz, 2H), 2.03 ppm (s, 6H); FTIR (KBr): $\tilde{\nu} = 3450$ (m), 1338(s), 1273(vs), 1189(s), 1109(vs), 1055(m), 989(s), 891(m), 802(m), 702 cm⁻¹(m); HR MS (ESI): *m/z* calcd for $C_{25}H_{16}F_6N_2S_2$: 523.0732 [L + H]⁺; found: 523.0746.

Preparation of gel CCG-1

A solution of O-3-PyFDTE in DMSO (0.05 mol L⁻¹, 0.2 mL) and a solution of $[Pd(NO_3)_2]$ in DMSO (0.025 mol L⁻¹, 0.2 mL) were mixed with the aid of ultrasonic vibration for 2 min to obtain a homogeneous solution. The resulting solution was left to stand at room temperature for about 10 h to form the gel CCG-1.

Rheological measurements

Rheological measurements $^{\scriptscriptstyle [35]}$ were studied by using a AR-G2 stress-controlled rheometer (TA Instruments) equipped with steel parallel-plate geometry (40 mm diameter). The gap distance was fixed at 250 µm. A solvent-trapping device was placed above the plate to avoid evaporation. All measurements were made at room temperature. Strain sweep at a constant frequency (6.28 rad s⁻¹) was performed in the 0.005-1000% range to determine the linear viscoelastic region of the gel sample. The frequency sweep was obtained from 0.1 to 100 rad s^{-1} at a constant strain of 2%, within the linear regime determined by the strain sweep. A thixotropic study was conducted to examine the recovery behavior of the gel after the strain sweep. The recovery of the storage modulus of the destroyed gel was monitored at a constant frequency (6.28 rad s^{-1}) under a low strain (2%) just after the strain sweep progress. The storage modulus G' and the loss modulus G'' were recorded as functions of time in the recovery processes. The cycle of deformation and recovery had two steps: 1) Deformation: A constant oscillatory strain (500%) that was enough to destroy the gel was applied to the fresh gel in the sample holder for 10 s. The frequency of the measurement was 6.28 rad s^{-1} ; 2) Modulus recovery in a time sweep: The recovery of the storage modulus was monitored at a constant frequency (6.28 rad s^{-1}) under a low strain (2%) within 20 s. G' and G'' were recorded as functions of time in both the processes.

Acknowledgements

We acknowledge the 973 Program (2012CB821701), the NSFC (21103233, 21273007, 21350110212 and 91222201), the NSF of Guangdong Province (S2013030013474), the Program for New Century Excellent Talents in University (NCET-13-0615), and the RFDP of Higher Education of China (20120171130006) for support.

Keywords: coordination cages · coordination modes palladium · photochromism · supramolecular gels

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Received: December 18, 2014 Published online on ■■ ■, 2015

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Metal-organic cages were utilized as building units for the first time to generate supramolecular gels, providing a synthetic approach to cavity-containing gels that display multi-responsiveness towards environmental physical and chemical stimuli (see figure).



Cage Compounds

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Creating Coordination-Based Cavities in a Multiresponsive Supramolecular Gel



Porous Materials

Cavities on different molecular levels, from molecular containers to macroscopic porous materials, have many potential applications. In their Full Paper on page ff., J. Zhang, C.-Y. Su, and co-workers describe an assembly approach to multiresponsive supramolecular gels by integrating photochromic metal–organic cages as predefined building units into the supramolecular gel skeleton, providing a new approach to create cavities in gels. Such supramolecular gels consisting of porous molecules may be developed as a new type of porous materials.