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COMMUNICATION

A responsive supramolecular metallogel constructed by coordination-driven self-assembly of a crown ether-based [3]pseudorotaxane and diplatinum(II) acceptor

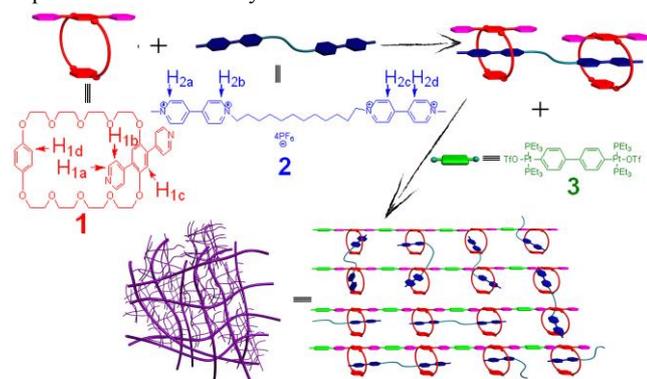## Hao Xing, Hu Wang, Xuzhou Yan[*] and Xiaofan Ji[*]

Herein, a stimuli-responsive supramolecular metallogel was prepared by orthogonal coordination-driven self-assembly of a crown ether-based [3]pseudorotaxane and 180° organic di-Pt(II) acceptor.

Supramolecular materials, whose components are reversibly brought together *via* noncovalent interactions, such as hydrogen bonding,[1] π–π interactions,[2] host–guest interactions,[3] and metal coordination,[4] *etc.* have recently attracted widespread attention as novel functional materials. Endowed by the dynamic and reversible nature of noncovalent interactions, supramolecular materials not only possess traditional materials properties but also exhibit some unique characteristics that are unavailable by their covalent counterparts, such as stimuli-responsiveness, self-healing and degradability, which make them suitable for smart devices and matter with various potential applications.[5] As a unique subject of self-assembled supramolecular materials, supramolecular gels which derive from the non-covalent self-assembly of low-molecular-weight organic compounds play a significant role in our daily life ranging from commercial products like hair gel and contact lenses to drug delivery for medical purposes.[6] Particular attraction of supramolecular gels to scientists lies in their reversible gel-sol transitions upon various external stimuli, including temperature, pH, sonication oxidation, addition of anions or cations, and so on.[7] Moreover, incorporating of metal centers into gel systems not only endows these soft materials with fascinating and peculiar characteristics of metal-complexes which can hardly be achieved by traditional organic gelators, but also provides a powerful driving force *via* metal–ligand interactions to induce the formation of functional gels.[8] Thus, there is a growing concern on the design and preparation of supramolecular metallogels in recent years.

Generally, a supramolecular gel can be regarded as a three dimensional network consisting of numerous fibers which connected by noncovalent interactions.[6,7] The fibers therein usually refer to linear supramolecular arrays, therefore, in most of previous studies, the formations of linear supramolecular polymeric arrays are necessary for the preparation of ultimate supramolecular gels. Among various self-assembly methods for the gelation, orthogonal self-assembly is a more powerful one

because it combines multiple noncovalent interactions to direct the desired soft matter outcome. For example, Huang and co-workers reported a multi-responsive, shape-persistent, and elastic supramolecular polymer network gel constructed by orthogonal self-assembly in 2012.[9] In this paper, a linear supramolecular polymer was prepared initially by the self-assembly of a heteroditopic monomer which contains a 1,2,3-triazole group between a benzo-21-crown-7 host and a dialkylammonium salt guest moiety, and then a cross-linker, PdCl₂(PhCN)₂, was added to make a cross-linked supramolecular polymer network based on the metal-coordination between 1,2,3-triazole group and palladium(II). More recently, Yin and co-workers reported a multiple-responsive self-healing supramolecular polymer gel network on the basis of multiple orthogonal interactions.[10] Based on the metal–ligand coordination interactions between terpyridine and Zn(OTf)₂ and the host–guest interactions between DB24C8 and dibenzylammonium salt (DBAS), a linear supramolecular polymer was constructed firstly and the ultimate supramolecular gel was then formed by continuous addition of PdCl₂(PhCN)₂ to cross-link the linear supramolecular polymer by coordinating with triazole units. These two elegant examples represent the orthogonal construction of functional supramolecular metallogels with complicated design. However, the initial preparation of linear supramolecular polymers requires time-consuming organic synthesis. In our previous studies, we explored the orthogonal crown ether-based host–guest interactions and Pt–N coordination bonds to construct responsive linear and cross-linked supramolecular polymers.[11] In these cases, we realized highly efficient construction of advanced supramolecular structures by orthogonal self-assembly of simple building blocks in one pot, which can avoid tedious organic synthesis to some extent. Because metal–ligand interactions can endow the resulting materials with various coordination geometries, strong yet tunable coordination abilities, photophysical, and redox properties, we are interested in the preparation of novel supramolecular metallogels based on the combination of host–guest molecular recognitions and metal–ligand bonding in an orthogonal way in one pot. Compared with previous strategies, this new orthogonal self-assembly approach is more convenient in synthetic procedure. Therefore, investigating and expanding

the scope of this new approach may have huge influences on supramolecular chemistry and materials science.

Scheme 1. Chemical structures of **1**, **2** and **3** and cartoon representation of the formation of a 3D supramolecular network.

Herein, we report a stimuli-responsive supramolecular metallogel, which is constructed by coordination-driven self-assembly of a crown ether-based [3]pseudorotaxane and 180° organic diplatinum(II) acceptor. A [3]pseudorotaxane was first prepared based on the well-known host–guest interactions between bis(*p*-phenylene)-34-crown-10 (BPP34C10) and paraquat (*N*,*N*'-dimethyl-4,4'-bipyridinium), which forms a 1:1 threaded structure.[12] Since the BPP34C10 derivative host **1** contains two pyridyl groups, it can also act as ligands for coordination with metal acceptors. After the addition of a 180° diplatinum(II) acceptor **3** into the [3]pseudorotaxane solution, a 3D supramolecular polymeric network simultaneously formed which is responsible for the observed gelation (Scheme 1). Taking advantages of the reversibilities of host–guest and metal–ligand interactions, this supramolecular gel displays interesting gel-sol transitions in response to multiple stimuli. It is worth noting that placing the three precursors in one pot will also result in the immediate gelation, demonstrating the power of this orthogonal procedure.

Initially, the [3]pseudorotaxane was prepared and various techniques were performed to confirm the formation of the [3]pseudorotaxane. Mixing of **1** (5.00 mM) and **2** (2.50 mM) in acetone-d_6 resulted in the formation of the designed [3]pseudorotaxane. In the ^{1}H NMR spectrum of the solution of **1** and **2** (Fig 1), obvious upfield shifts in the signals of the aromatic protons of **1** ($H_{1a–d}$) and **2** ($H_{2a–d}$) were observed, indicating that π−stacking occurs between these electronically complementary aromatic rings and further demonstrating the complexation between the host **1** and the guest **2** (Fig 2b).[13] The association constant (K_a) between BPP34C10 and paraquat moiety was determined to be 7.04×10^2 M^{-1} and the host−guest interaction was proven to be fast on the NMR timescale in our previous research.[11d] From the NOESY NMR spectrum of the solution of **1** and **2** (Fig. S3, ESI†), correlation signals were observed between protons $H_{2a–d}$ of the paraquat moiety and aromatic protons $H_{1a–d}$ of the crown-ether host. Moreover, the correlation signals between ethyleneoxy protons of the host and protons $H_{2a–d}$ of the guest were also observed, proving that the paraquat moiety really thread through the cavity of the crown-ether host.[14] What's more, the UV–vis spectroscopy further confirmed the formation of the [3]pseudorotaxane since obvious absorption spectral changes

induced by charge transfer interactions between electron-rich aromatic rings of the host and electron-poor pyridinium rings of the guest were observed (Fig. S4, ESI†), which was in accord with the previous studies of crown ether-based molecular recognition.[15]
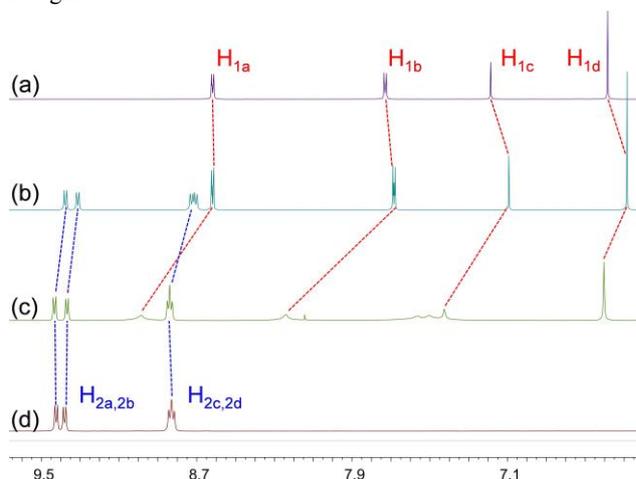

Fig. 1 Partial ^{1}H NMR spectra (500 MHz, acetone-d_6, 293 K): (a) 5.00 mM **1**; (b) 5.00 mM **1** + 2.50 mM **2**; (c)5.00 mM **1** + 2.50 mM **2** + 5.00 mM **3**; (d) 5.00 mM **2**.

Then, the conversion from low-molecular-weight aggregates to 3D supramolecular polymeric network was investigated. Upon addition of di-Pt(II) acceptor **3**, the pyridine protons of host **1** exhibited downfield shifts (H_{1a} and H_{1b}), resulting from the loss of electron density upon coordination of the pyridine N atom with the Pt(II) center (Fig 1c), demonstrating the formation of metallosupramolecular network driven by metal-coordination between the [3]pseudorotaxane and the acceptor **3**. Moreover, the signals of the protons of **1** exhibited significant broadening which at the same time indicated the formation of a cross-linked supramolecular polymeric network. To further substantiate the formation of supramolecular network, 2D diffusion-ordered ^{1}H NMR spectroscopy (DOSY), a convenient and reliable method to test the dimensions of polydispersed supramolecular aggregates, was performed (Fig. S5 and S6, ESI†). For a mixture of **1** and **2** at 5.00 mM, the measured weight average diffusion D value was 1.03×10^{-9} m^{2}s^{-1}, but when 1.00 equiv of **3** was added to the solution, a decrease in the diffusion coefficient value from 1.03×10^{-9} to 2.65×10^{-11} m^{2}s^{-1} was observed, which can be explained by the fact that the supramolecular networks have greater obstacles in molecular motion and further lead to a lower measured weight average diffusion coefficient. And according to the Stokes-Einstein relation, the average degree of polymerization was estimated (Fig. S5 and S6, ESI†).[16] DLS experiment, a technique especially useful in determining the size distribution profile, structure formation and interactions of supramolecular systems, was conducted to study the size distributions of the assemblies. The average hydrodynamic diameter (D_h) of [3]pseudorotaxane was determined to be 1.74 nm and after an equimolar di-Pt(II) acceptor **3** was added, the corresponding D_h value increased obviously to 712 nm, which are consistent with the above-discussed DOSY experiments (Fig 2). This data was not used to further calculate the degree of the polymerization and the polydispersity because the spherical model is not suitable for

our system. These two observations simultaneously proved an increase in the average aggregation size owing to the conversion from low-molecular-weight aggregates to the 3D supramolecular network. In order to demonstrate the orthogonal procedure of this supramolecular network, we prepared linear coordination polymer and performed the experiment *via* the addition of increasing amounts of the bisparaquat to the coordination polymer. Stirring an equimolar mixture of **1** and **3** in acetone 30 minutes resulted in the formation of coordination polymer, which was comfirmed by ^{1}H NMR spectra (Figure S8b). Upon adding successive amounts of the bisparaquat, the aromatic protons of **1** (H[1c]) and **2** (H[2a-d]) gradually shifted upfield due to the host−guest interaction (Figure S8b-f and Figure S9). After adding 0.5 equiv of **2**, the ^{1}H NMR spectrum was the same as the treatment of **1** + **2** mixture with the platinum. The best demonstration of the power of this orthogonal procedure is to employ a one-pot self-assembly. Just mixing a 2:1:2 ratio of three different components **1**, **2**, and **3** also produces the unique 3D supramolecular polymeric network.
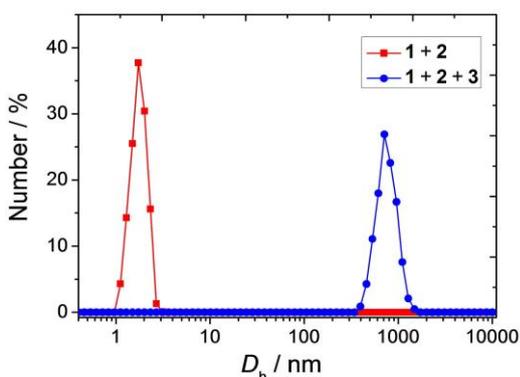

Fig. 2 Size distributions of **1** + **2** and **1** + **2** + **3**. *c* = 5.00 mM.

The morphologies of the supramolecular xerogels prepared by freeze-drying methodology were examined by scanning electron microscopy (SEM). As shown in Fig. 3, the electron microscopy images of the xerogel give a nanoribbon morphology which can account for the orthogonal noncovalent interactions to form entangled networks (Fig 3a). These results showed that the metal-coordination interactions between the [3]pseudorotaxane and **3** not only achieved the conversion from low-molecular-weight aggregates to the 3D supramolecular polymeric network, but also made an impact on the microscopic nature of the resultant supramolecular metallogel.[17]
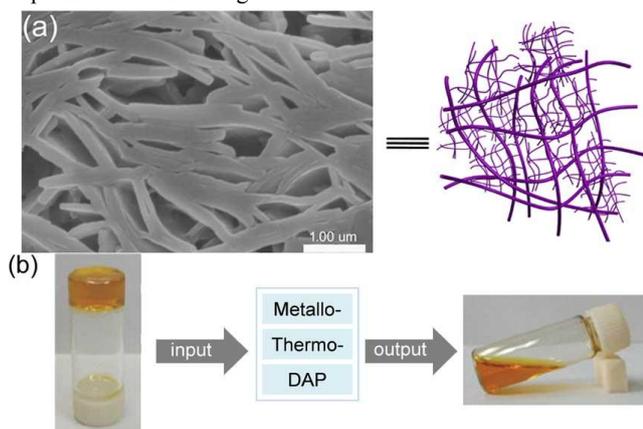

Fig. 3 (a) SEM image and cartoon representation of the supramolecular

gel (b) The gel-sol transitions of the supramolecular gel triggered by different stimuli: Metallo- means adding TBABr, Thermo- means heating and cooling, DAP means adding a competitive guest 2,7-diazapyrenium (DAP).

Supramolecular gels that can response to external stimuli are always attractive. It is well known that the crown ether based host–guest interactions could be controlled by temperature.[18] Therefore, heating and cooling can result in a reversible gel-sol transition in this obtained supramolecular metallogel (Fig 3b) and the gel-sol transition temperature was about 313K at the concentration of 30 mM In our previous work, we found that 2,7-diazapyrenium (DAP) derivative have a better binding ability with BPP34C10 that can expel the paraquat unit from the cavity of host **1**,[11d] so an gel-sol transition was also achieved by adding this competitive guest and this process was not reversible(Fig 3b). Furthermore, the gel-sol transition can be realized by taking advantage of the dynamic nature of Pt-N bonds, which can control the disassembly of supramolecular polymer backbones.[19] Upon adding 1.00 equiv of tetrabutylammonium bromide (TBABr) (relative to the di-Pt(II) acceptor **3**) into the supramolecular gel, the gel gradually collapsed and ultimately became a yellow suspension with precipitate at the bottom (Fig 3b). It is because adding TBABr to the solution not only caused the breakage of Pt-N bonds but also made bispraquat **2** insoluble in acetone because of the ionic exchange from PF[6]− to Br− and this also made the sol-gel transition irreversible. The ^{1}H NMR also confirmed the destruction of the former gel and the precipitation of paraquat **2** since there was no signals for bisparaquat **2** (Fig. S7, ESI†). Thus, the three distinct stimuli mentioned above can be used as effective inputs to adjust the gel-sol transitions of the supramolecular gel obtained by the self-assembly of the [3]pseudorotaxane and diplatinum(II) acceptor, reflecting the dynamic nature of this novel supramolecular gel system.

In summary, based on the coordination-driven self-assembly of a crown ether-based [3]pseudorotaxane and 180° organic diplatinum(II) acceptor, a supramolecular metallogel was efficiently constructed. What is particularly exciting is that the obtained gel is exclusively derived from the non-covalent self-assembly of low-molecular-weight building blocks in a noninterfering orthogonal way. The 3D supramolecular network was well confirmed by a combination of various techniques, including ^{1}H NMR, DOSY, and DLS, *etc*. Moreover, the supramolecular gel shows thermo-, competitive guest- and metallo-induced gel-sol transitions, which lay a foundation for further applications as advanced intelligent materials. The unification of host−guest chemistry, coordination-driven self-assembly, and supramolecular polymerization in an orthogonal way in this *communication* defines a method to the engineering of soft matter with unique stimuli-responsiveness. Given the rich chemistry of metal-coordination complexes and host−guest complexes, we expect this methodology to unlock fascinating designs incorporating metal centers into functional supramolecular materials.

Notes and references

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China. Fax: +86-571-8795-3189; Tel: +86-571-8795-3189; E-mail: xzyan@zju.edu.cn; xiaofanji@zju.edu.cn

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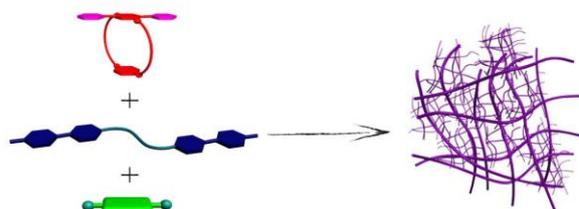
Text:

A stimuli-responsive supramolecular polymeric metallogel was prepared by orthogonal coordination-driven self-assembly of a crown ether-based [3]pseudorotaxane and 180° organic di-Pt(II) acceptor.