

Metallogel Self-Assembly |Hot Paper|

Metallogels Self-Assembled from Linear Rod-Like Platinum Complexes: Influence of the Linkage

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Abstract: Two linear rod-like platinum complexes, which only differed in the linkage, were prepared. They both self-assemble into metallogels in nonpolar solvents; however, a very big contrast was observed. Unexpectedly, a much weaker gel was acquired upon replacing the ester linkage by an amide group. The intermolecular hydrogen bonding offered by the amide motif leads to a different stacking fashion and mechanism. The results demonstrated herein contribute to the rational design of metallogels as well as other functional supramolecular materials.

As an important part of functional materials constructed through self-assembly, supramolecular gels have been a research hotspot recently.^[1] The gels are formed by hierarchical actions of noncovalent forces organizing a three-dimensional network from low-molecular-weight gelators to immobilize the solvents. The dynamic nature of noncovalent interactions gives the gels intriguing properties such as stimuli responsiveness and self-healing,^[2] which opens a much wider field of application than for traditional polymer networks. So far, supramolecular gels have been researched for soft electronics, biomaterials, sensors, drug delivery, crystal growth media, catalysis, and so on.^[3]

Among the vast explored supramolecular gels, metallogels, formed either from metal-ligand interactions or metallogelators, have attracted increasing interest owing to the unique properties of metal centers.^[4] Though there are multiple choices of metal species, which have been varied from main group to transition metals, platinum-based gelators have received particular attention. The square-planar geometry is well suited to supramolecular interactions and platinum complexes

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tors have attracted significant amounts of work. Undoubtedly, the most outstanding type is the terpyridyl platinum-acetylide complexes explored by Yam and other groups.^[5] The Pt–Pt and π - π interactions render the aggregated metallogels with fascinating spectroscopic and luminescence properties. Besides these charged gelators, linear rigid-rod platinum-acetylides have also attracted attention lately.^[6] The neutral state facilitates the gelation of nonpolar solvents and some of the metallogels show excellent emissive behaviors.^[7] Very recently, another emerging neutral-type complex, trans-bis(pyridine) dichloroplatinum(II) and its palladium(II) counterpart were also found to successfully self-assemble into metallogels. Metallophilic and $\pi - \pi$ interactions were the major driving forces for the gelators with long alkyl chains, yet weak C-H-O and C-H-Cl interactions also played an important role for the gelators with ethylene glycol chains.^[8]

often show rich luminescent properties. To date, platinum gela-

In this work, two similar *trans*-bis(pyridine) dichloroplatinum(II) type complexes, which only differ in the linking group, were prepared. The two complexes (Figure 1), namely **1-E** and



Figure 1. Chemical structures of the two complexes.

1-A, both have a rigid core and two long alkyl tails linked by ester or amide groups, respectively. The large and rigid platinum-containing core is ready for π -stacking and metallophilic interaction. In addition, as a common hydrogen-bonding motif, we intended to strengthen the gel by the introduction of amide groups. It should be noted that considerable amounts of *cis* isomers also formed at lower reaction temperatures (Figure S8 in the Supporting Information). The fact that the *cis* products were unable to gelate common solvents also

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points to the importance of the linear rod shape. For detailed synthetic work, see the Supporting Information.

1-E, 1-A both gelate nonpolar hydrocarbon solvents such as *n*-hexane, *n*-dodecane, and cyclohexane. However, the critical gelation concentration (CGC) differs significantly (Table S1 in the Supporting Information). 1-E almost behaves as a supergelator with a CGC about 1%, whereas 1-A shows poor gelating ability with a CGC about 5 times higher. This is quite uncommon as amide groups often play an important part in constructing supramolecular gels through intermolecular hydrogen bonding.^[9] In addition, there is another difference between the two gels: the *n*-hexane and *n*-dodecane gels of 1-E gradually shrunk once formed, but the gels of 1-A were stable (Figure S1 in the Supporting Information). The shrinkage indicated secondary organization and was avoided by using cyclohexane or a mixed solvent system of n-hexane and chloroform.^[10] In *n*-hexane/chloroform (v/v=5:1), **1-E** forms a transparent gel that is stable for weeks, whereas no gelation occurs for 1-A. Rheological measurements further confirmed the gel phases (Figure 2e). The storage modulus (G') was always larger than the loss modulus (G'') over the entire range of shear frequency, which revealed a typically solid-like gel nature. Even the gel of 1-E contained some chloroform and the values of G'and G'' indicated that the gel of **1-A** was much weaker than that of 1-E. The gel of 1-A failed to maintain its shape once taken out of the vessel, whereas the cyclohexane gel of 1-E showed good self-standing behavior (Figure 2 c, d).

In most cases, supramolecular gels consist of onedimensional fibrillar networks. The slightly diluted solutions of the gels also showed these morphologies, as revealed by TEM (Figure 3). Even so, differences between the gels were also evident. **1-E** gave straight bundles of fibers, whereas **1-A**



Figure 2. Images of the gels of **1-E** (a) and **1-A** (b) formed in cyclohexane. A self-standing cyclohexane gel of **1-E** (c) and the same one (d) loaded with a coin (about 6 g). e) Rheology properties of the two gels (34 mg mL^{-1}) in *n*-dodecane for **1-A** and *n*-dodecane/chloroform (v/v = 5:1) for **1-E**.



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Figure 3. TEM images of 1-A (a) and 1-E (b,c) cast from diluted cyclohexane gels (1 mm). The scale bars are 200 nm.

aggregated into a twisted and highly entangled network. It should also be emphasized that the fibers of **1-A** adopt clear helicities. To further explore the origins of the supramolecular gels, samples from casting highly diluted solutions of the two complexes have been studied. As expected, very thin nanofibers were observed in both circumstances (Figure S2 in the Supporting Information). We found that the diameters of the thinnest fibers were about 4 nm, just consistent with the molecular length of the complex. Thus, a single nanofiber was constructed from one-dimensional stacking of each molecule.

To explain the big contrast of gelation ability, UV/Vis spectroscopy was used to monitor the supramolecular polymerization mechanism. Solvent-dependent UV/Vis spectra revealed the detailed disaggregation processes (Figure 4). With increasing fractions of chloroform, disaggregation occurred for both gels. On going from monomeric to fully aggregated states, the band of **1-A** gradually lost its intensity and fine structure. A blueshifted peak emerged at 320 nm and a redshifted one appeared at 372 nm, which was reminiscent of the H-type aggregates reported by Würthner and co-workers.^[11] The two peaks were ascribed to face-to-face (320 nm) and rotational stacking (372 nm) of the chromophores. Such a helical aggregation

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Figure 4. Solvent-dependent UV/Vis spectra of **1-E** (a) and **1-A** (b). The total concentration is 7.5 μ M and the arrows indicate the change upon adding chloroform to the cyclohexane solution. c) Plot of aggregated fraction as a function of solvent composition (379 nm for **1-E** (square) and 336 nm for **1-A** (circle)). The line indicates a sigmoidal fit for the data of **1-A**.

model has also been confirmed by the TEM observations and circular dichroism (CD) spectra (Figure S3 in the Supporting Information). The aggregation process of **1-E** was different. The primary band maintained its intensity with some increase and decrease of the other peaks. The isosbestic point at 343 nm also indicated an equilibrium point between the monomeric and aggregated species. Most importantly, a new band at 379 nm emerged and increased remarkably upon further aggregation. The sharp redshifted band is characteristic of slipped J-type aggregates.^[12] The existence of d–d interactions from the metal orbitals is unlikely here as the transition bands are often broad and weak.^[8a,d,13]

Absorbance at two representative wavelengths was used to monitor the aggregation fraction.^[14] As shown in Figure 4c, aggregates of 1-A were able to tolerate chloroform much better than those of 1-E. Moreover, the two sets of data varied in shape. The data points for 1-A could be fitted by a sigmoidal curve, which pointed to an isodesmic mechanism. However, 1-E exhibited a distinct critical concentration at a chloroform volume fraction of about 5%, which pointed to a highly cooperative model. Concentration dependent work has also confirmed the highly cooperative character of 1-E (Figure S4 in the Supporting Information). As a highly aggregated state was observed even at 10^{-7} M in pure nonpolar solvents, the mixed solvent system *n*-hexane/chloroform (v/v = 5:1) was used. The spectra of 1-E showed good agreement with the Beer-Lambert law when the concentration was below 9×10^{-5} M, whereas a new band at 379 nm suddenly appeared and increased rapidly upon further concentration. The new band could well represent the aggregated species. Plotting the aggregation fraction gave a nonsigmoidal shape, which also pointed to a highly cooperative supramolecular polymerization process. The data points were fitted manually to a dimer model and it is highly plausible that 1-E dimerizes and elongates in a slipped fashion. The aggregation model of 1-A was also confirmed by concentration dependent work (Figure S5 in the Supporting Information).

For direct comparison, UV/Vis and fluorescent spectra of both complexes in the molecular dissolved and aggregated states were combined (Figure S6 in the Supporting Information). The amide linker barely influences the absorption properties of the monomers as similar shapes and extinction coefficients were observed for the dissolved state of both 1-A and 1-E. However, the spectra of the aggregates were quite different. 1-E was characterized by a new absorbance band at 379 nm, whereas the absorbance of 1-A was strongly reduced and broadened. Weak ligand-centered emissions were observed for the chloroform solutions. Owing to the suppressed nonradiative decay process in the aggregated state, the cyclohexane solutions showed some enhanced emissions while maintaining the shapes.

Concentration-dependent ¹H NMR is a powerful method to monitor hydrogen bonding and π -stacking during self-assembly. We carefully chose the proper solvents to avoid signal broadening (Figure S7 in the Supporting Information). In a solvent mixture of $[D_{12}]$ cyclohexane/CDCl₃ (v/v = 3:8), the aromatic protons of **1-E** showed a distinct upfield shift upon increasing concentration. **1-A** was found to self-assemble in pure CDCl₃. An upfield shift was also observed for the aromatic protons, whereas the amide signal undertook a downfield shift of 0.33 ppm. An upfield shift generally implies π - π stacking, whereas a downfield shift indicates hydrogen bonding.^[15] Thus, π - π stacking is involved in both aggregation processes and **1-A** also adopts strong intermolecular hydrogen bonding.

The wide-angle X-ray diffraction (WAXD) study on the two xerogels further supports the existence of the two different stacking fashions (Figure 5). In the wide-angle region, though a diffraction peak related to π - π stacking was observed in both circumstances, the difference was evident. For the amide-

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Figure 5. WAXD spectra of the two xerogels.

linked molecule, **1-A**, a very broad peak centered at d=0.40 nm indicated a weak stacking and a broad distribution of the aggregates. However, the π - π stacking peak of **1-E**, centered at d=0.37 nm, was a much sharper one. The longer π - π stacking distance of **1-A** revealed that the hydrogen bonding has weakened the aromatic interactions.

Based on the above results, we can draw some conclusions. Though the two gelators both self-assemble into 1-D stacks, there are some differences. Driven by π - π interactions, **1-E** packs into slipped stacks through a highly cooperative mechanism. But for **1-A**, the incorporation of amide groups introduces the possibility for hydrogen bonding. Thus, intermolecular hydrogen bonding and π -stacking give a rotational packing of the chromophores. The parallel packing surely encounters more repulsion from the metal center and, thus, loose helical aggregates form (Figure 6). Although there are many factors



Figure 6. Possible molecular arrangements of 1-E (left) and 1-A (right).

related to supramolecular gelation, some clear points are highly plausible to explain the big contrast between the two gels. As the aggregates of **1-E** are more tightly stacked, as revealed by WAXD, the fibers are more rigid, which strengthens the gel phase. Moreover, a highly cooperative mechanism proves to be an advantage as it avoids the formation of small oligomers and gives a narrow polydispersity for the highmolecular-weight supramolecular polymers.^[16]

Supramolecular gels form through hierarchical organization of the gelators. In this process, some noncovalent interactions are required and often hydrogen bonding is the most essential factor. As a common linkage, amide groups are usually capable of promoting gelation by forming intermolecular hydrogen bonds. But our study here demonstrates a contrary case. Compared with the ester-linked molecule, the amide group alters the aggregation model and weakens the gelation ability remarkably. Our work highlights a big difference in aggregation resulting from a tiny structural change, which will help the rational design of functional supramolecular assemblies. In a more specific aspect, our findings will shed some new light on the construction and optimization of platinum-based π -functional materials.

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