Metallogels Self-Assembled from Linear Rod-Like Platinum Complexes

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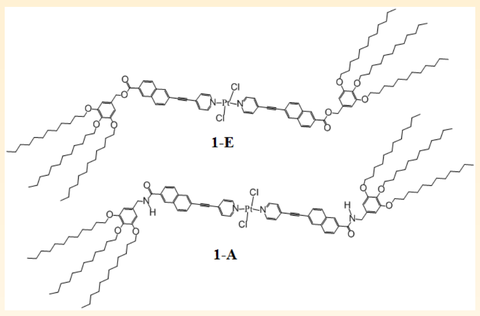
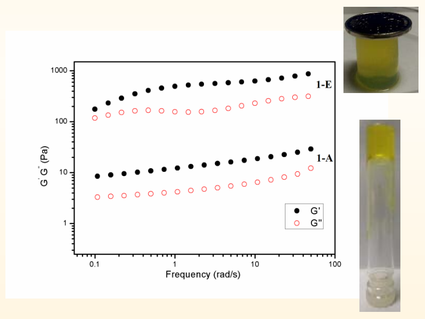
Introduction

As an important part of the functional materials constructed through self-assembly, supramolecular gel has been a research hotspot recently. Starting from low molecular weight gelators, hierarchical actions of noncovalent forces organize a three dimensional network to immobilize the solvents. The dynamic nature of noncovalent interactions offers the gel intriguing properties such as stimuli responsive and self-healing, which gives a much wider field of application than the traditional polymer networks. So far, supramolecular gels have been researched for soft electronics, biomaterials, sensors, drug delivery, crystal growth media, catalysis and so on. Among the vast explored supramolecular gels, metallogels, formed either from metal-ligand interactions or metallogelators, have attracted increasing interests owing to the unique properties from metal centers. Though there are multiple choices of metal species varied from main group to transition ones, platinum based gelators have received a particular attention. The square planar geometry is well suited to supramolecular interactions and platinum complexes often show rich luminescence properties.



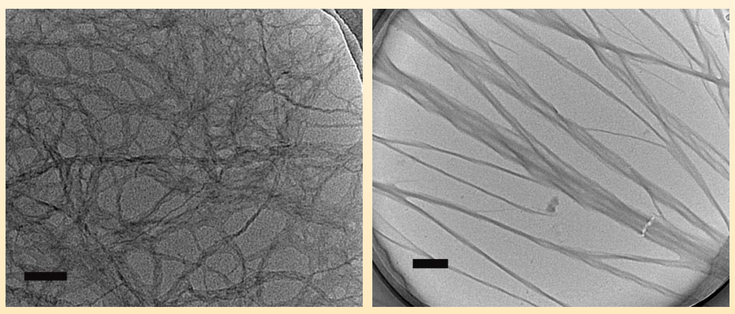
In this work, two similar trans-bis(pyridine) dichloroplatinum(II) type complexes which only differ in the linking group were prepared. The two complexes, namely **1-E** and **1-A**, both have a rigid core and two long alkyl tails linked by ester or amide groups respectively.

Experiments and Data

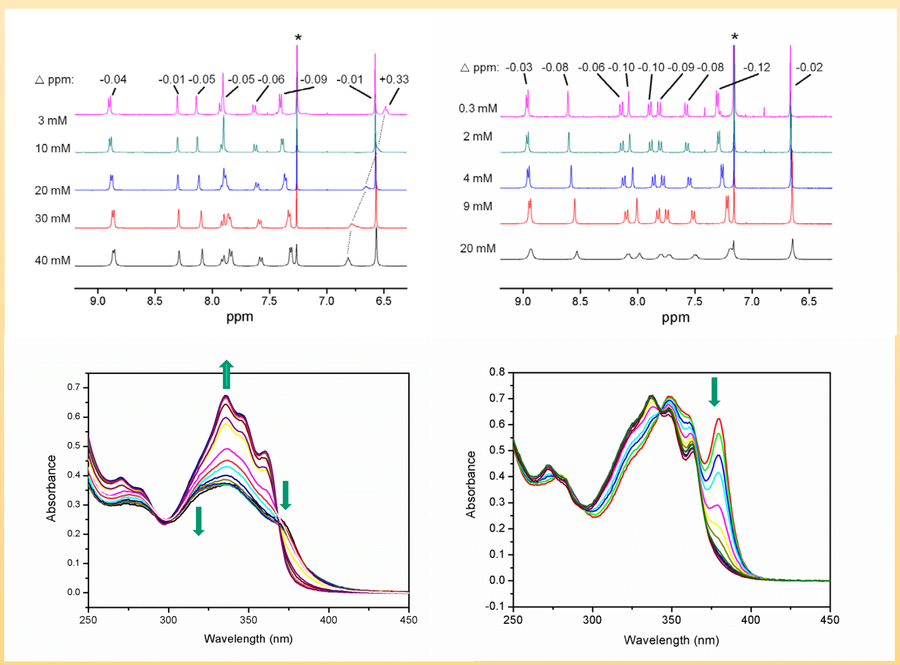


Solvent	CGC(1-E)	CGC(1-A)
n-hexane	7.7	43
n-dodecane	6.2	34
n-hexane/chloroform (v/v=5:1)	15	P
cyclohexane	8.8	80

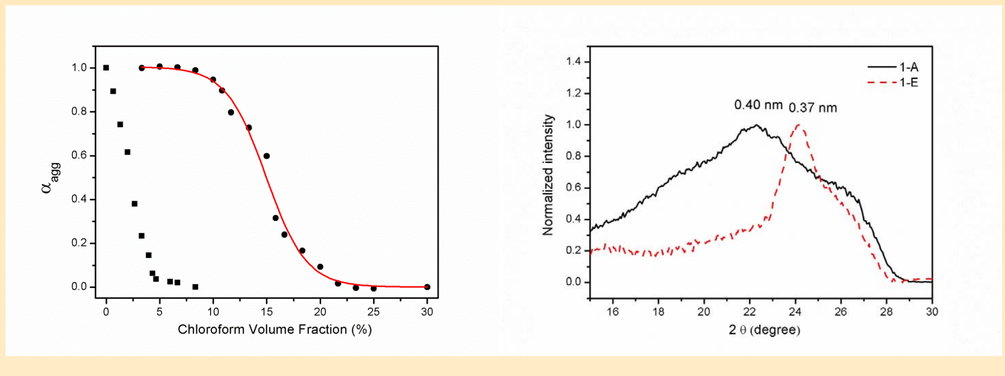
Gelation property: Rheology of the two gels and critical gelation concentration (CGC) of the two complexes.



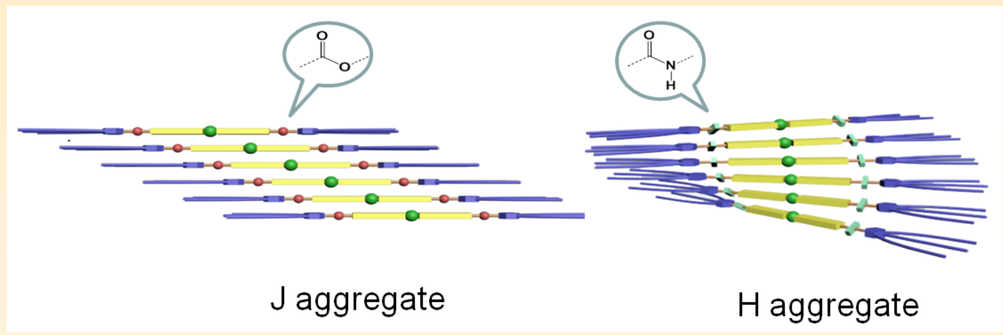
Morphology: TEM images of diluted gels of 1-A (left) and 1-E (right).



Self-assembly process: Concentration dependent ^{1}H-NMR and solvent dependent UV-vis spectra of 1-A (left) and 1-E (right).



Self-assembly mechanism: Left: UV-vis spectra change monitored at 337 nm (1-A) and 380 nm (1-E) and an isodesmic fit of the data of 1-A. Right: WAXD of the two xerogels.



Molecular arrangements

Methods

- Synthesis: ^{1}H, ^{13}C -NMR, MALDI-TOF-MS, Elemental Analysis.
- Supramolecular polymerization mechanism: ^{1}H–NMR, TEM, WAXD, UV-Vis, PL and CD spectra.
- Morphology of the self-assemblies: TEM, SEM .
- Mechanical strength: Rheology.

Discussion and Conclusion

- The two complexes self-assemble into one dimesional nanofibers through π-π stacking and other interactions, as evidenced by concentration dependent ^{1}H-NMR. The one with amide group adopts a helical H-type packing while the ester counterpart arranges in a slipped J-type fashion.
- Hydrogen bonding is important to fix the chromophores to stack in a face to face manner but not essential to strengthen the metallogels. The gel with hydrogen bonding interactions here is much weaker than that of the ester one.
- A cooperative mechanism is important to construct strong metallogels as it avoids the formation of oligomers and possesses a narrow dispersity of supramolecular polymers. Besides, the tight packing of the gelators is also very important.

Publication or other achievement

Metallogels Self-Assembled from Linear Rod-Like Platinum Complexes: Influence of the Linkage.
Mingming Chen, Chengsha Wei, Xibo Wu, Majid Khan, Ningdong Huang, Guobin Zhang, Liangbin Li.
Chem. Eur. J. Revised

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