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A Highly Selective, Hg\(^{2+}\) Triggered Hydrogelation: Modulation of Morphology by Chemical Stimuli

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We report the first Hg\(^{2+}\) selective hydrogelation by 4’-[4-(4-aminophenyl)phenyl]-2,2’-6’,2’’-terpyridine. The gel showed remarkable response towards specific chemical agents such as benzo-18-crown-6 ether and K\(^+\) which enabled extensive modulation of the gel morphology.

In the past few decades, self-assembly of small molecules has been extensively used as an efficient strategy to build and modulate nanostructures. Low molecular weight supramolecular hydrogels have in particular found myriad applications in fields such as organic-inorganic hybrid materials,\(^1,2\) medicines,\(^3\) optoelectronics.\(^4\) One of the most important and desirable feature of these gels is the dynamic nature of the assemblies which allows structural modulations at the molecular level. Numerous such functional materials have been reported in recent literature where it was possible to modify the physical properties by applying external stimuli such as pH,\(^5\) photons,\(^6\) chemical agents.\(^7,8\) This has also encouraged the use of such responsive supramolecular assemblies as potential indicator systems for changes in the immediate environment.\(^9\)

Among various stimuli applied to modify gel behavior, metal ions have been one of the most common regulators. On several occasions, introduction of metal ion in the gelator media was shown to have triggered long range self-assemblies which ultimately resulted in the formation of 3D-gel network.\(^10\) In some cases, gelators had also been covalently modified with specific metal-binding motifs to impart selectivity.\(^11,12\)

Terpyridines are one of the most extensively used ligands to complex transition metal ions and had often served as a building block for supramolecular gel systems.\(^13-15\) The easy tunability of its physical properties by varying the metal ions made it a very promising prospect for such assemblies. However, due to their universal coordination ability the terpyridines lack the binding specificity towards any particular metal ion leading to a situation that the gelation process is not metal ion specific. Herein, we report formation of a supramolecular hydrogel of 4’-[4-(4-aminophenyl)phenyl]-2,2’-6’,2’’-terpyridine L in presence of Hg\(^{2+}\) ion. The gel was formed under slightly acidic conditions and showed a remarkable selectivity towards Hg\(^{2+}\) in terms of the gelation behavior. To the best of our knowledge, this is the first report of a hydrogelation triggered specifically by divalent mercury ion. In the course of detailed investigations we observed that significant control over the gel morphology could be achieved by addition of specific reagents, namely benzo-18-crown-6 (B18-C-6) and K\(^+\) ions. Ligand L was synthesized by the Suzuki cross-coupling reaction between 4’-[4-bromophenyl]-2,2’-6’,2’’-terpyridine \(^{16}\) and 4-aminophenylboronic acid pinacol ester 2 in dimethoxyethane solvent in the presence of Na\(_2\)CO\(_3\) using Pd(PPh\(_3\))\(_4\) as catalyst (Scheme 1).

Ligand L was solubilized in aqueous solution of 0.2 N HCl. At this pH, the interactions (hydrogen bonding and electrostatics) between the partially protonated ligand (L) units were not able to form any kind of self-organized structures in aqueous media. However, the coordination of ligand L to metal ions was perceived to cause significant charge polarization in complexes, leading to stronger intermolecular interactions and self-assembly. Based on this, several metal ions were tested and disappointingly most of the earth alkaline and transition metal complexes (Fig. 1) precipitated out from the solution. However, Hg(II) showed remarkable ability to form hydrogels when added to aqueous solution of L (Fig. 1). Given the lack of any specific Hg(II) binding motif on ligand L, the high degree of selectivity of the gelation process towards Hg(II) was indeed intriguing.

Different ligand to Hg\(^{2+}\) ratios were studied in order to optimize the gelation process and hydrogelation occurred at Hg\(^{2+}\):L ratio of 1:1. However, a visibly stronger gel was obtained when Hg\(^{2+}\) to ligand ratio was increased to 2:1 and thus this ratio was used for further studies. The formation of the gel was found to be hampered in the presence of other divalent metal ions in combination with Hg\(^{2+}\) (see ESI†). Though the reasons for this unusual selectivity are not perfectly understood, it can be assumed that the large size of the divalent mercury cation plays...
in the presence of Hg\(^{2+}\) (and chloride anions) was thermo-reversible and found to be thixotropic in nature. To better understand the morphological properties of the gel, morphology of the xerogel was elucidated by SEM (scanning electron microscopy) and TEM (transmission electron microscopy) techniques which revealed the structure of the gel matrix to consist of a uniform, dense network of very thin fibers (Fig. 2). The width of the fibers was determined by HRTEM to be \(\approx 10\) nm.

In order to explain the aggregation behavior, crystal structure of the HgCl\(_2\)\(\cdot\)L complex was analyzed. Since it was extremely difficult to obtain single crystals under the exact conditions that led to gelation, the hydrogel was dissolved in DMF and slowly evaporated to yield yellow plate-like single crystals of HgCl\(_2\)\(\cdot\)L. The mercury has distorted trigonal bipyramidal N\(\cdot\)Cl coordination (Fig. 3a). Apart from the exception of the benzene ring between the terpyridine domain and aniline moiety, ligand L was otherwise observed to be planar. Analysis of the crystal packing revealed the presence of strong \(\pi\cdots\pi\) interactions (3.26 Å) between the central pyridine ring of the terpyridine domain and the anilinic benzene ring of the adjacent complex. Additionally, moderate N-H\cdotsCl interactions (H\cdotsCl = 2.65 Å) (between the terminal Cl atom and adjacent anilinic H-atoms) were also found to be present in a dimeric motif (Fig. 3b).

From the crystal packing of the HgCl\(_2\)\(\cdot\)L complex it can be concluded that in the gel the partially protonated aromatic amines (gel forms under mildly acidic conditions) play a key role in the self-assembly process. A control gelation experiment was also carried out with 4\'-[4-(4-phenylphenyl)-2,2\'\'6,2\''-terpyridine \(\text{Hg}^{2+}\)(without the amine functionality). However, addition of Hg(II) to its 0.2 N HCl solution results immediate precipitation of the metal complex (see ESI\(^\dagger\)).

It was evident that manipulating the key interactions could in principle provide a certain degree of geometrical control over the aggregates which would indeed be advantageous in the formation of advanced soft materials. Actually Zhang et al., have recently demonstrated the use of different metal complexes to predetermine the dimensionality of intermolecular interactions, enabling the construction of nanofibers with single-molecule width \((3.1 \pm 0.1\) nm\).\(^{17}\)

In this context, we investigated how a crown ether, here B18-C-6, would modify the aggregation behavior of L in presence of Hg\(^{2+}\). Based on the ability of the crown ether to bind to the ammonium end of the complex and thus blocking of the growth of the fibrous assembly was envisaged. As expected the gel network collapsed after the addition of about 0.4 equivalents of B18-C-6. However, in the presence of 4.0 equivalents of K\(^{+}\), along with B18-C-6 in the acidic solution of L, addition of Hg\(^{2+}\) resulted in a visibly weaker gel (Fig. 4), presumably due to the stronger binding of K\(^{+}\) to the crown ether.

Fig. 1 From left to right 12 mM of (chloride salt of) Mg\(^{2+}\), Ca\(^{2+}\), Mn\(^{2+}\), Fe\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\) in 6 mM of L.

Fig. 2 a) TEM (inset: HRTEM of single fiber, scale bar 100 nm) and b) SEM image of hydrogel of 12 mM Hg\(^{2+}\) in 6 mM of L.

Fig. 3 (a) ORTEP plot of the molecular structure of HgCl\(_2\)\(\cdot\)L. Thermal ellipsoids are shown at 30% probability level. Selected bond distances (Å) and angles (°): Hg(1)-N(1) 2.395(7), Hg(1)-N(2) 2.373(5), Hg(1)-N(3) 2.437(7), Hg(1)-Cl(1) 2.436(3), Hg(1)-Cl(2) 2.461(2), Cl(1)-Hg(1)-Cl(2) 106.52(10), N(2)-Hg(1)-N(1) 68.6(2), N(2)-Hg(1)-N(3) 67.8(2); (b) The dimeric motif in the crystal packing of HgCl\(_2\)\(\cdot\)L.

Fig. 4 12 mM of Hg\(^{2+}\) in 6 mM of L in 1) excess KCl and 2.5 mM B18-C-6, 2) in absence of any additives; 3) 2.5 mM B18-C-6.
Since the gel properties predominantly depend on its morphology, it was interesting to probe the changes in the Hg\(^{2+}\)C-L xerogel structure with TEM. The TEM images show that while the nanofibrillar network was completely destroyed upon the addition of B18-C-6, it was partially restored in the presence of K\(^+\). However, when compared to the original gel, the nanofibers formed in the presence of crown-ether and K\(^+\) were found to be much shorter in length but at the same time appeared to be much thicker (20-30 nm).

The shorter and thicker fibers formed a loosely packed network which led to a visibly weaker gel. Further evidence for the gel morphology was obtained through the scanning electron microscopy (SEM) analysis (Fig 5). Both TEM and SEM analysis confirmed the observed changes in the morphologies of the hydrogels under specific chemical stimuli. This clearly proves the significantly altered interactions at the molecular level and allows control over the gel morphology in the nanoscale domain, a much desired property in novel material design.

In conclusion, 4'-[4-(4-aminophenyl)phenyl]-2,2',6',2''-terpyridine was shown to form a thermo-reversible, translucent, thixotropic, supramolecular hydrogel exclusively in the presence of Hg\(^{2+}\) under acidic conditions. The \(\text{N}_2\text{Cl}_2\) coordination in the HgCl\(_2\)-L complex was found to be imperative for gelation, an unusual and unprecedented example of Hg\(^{2+}\) selectivity. Other studied divalent transition metal cations did not from a gel on their own and further disrupted the gelation process when added in conjunction with Hg\(^{2+}\). Strong \(\pi\)-\(\pi\) interactions between the terpyridine units coupled with the salt-bridge interactions triggered by Hg\(^{2+}\) are likely to be the major driving force for the self-assembly process. The microscopy investigations revealed the gel structure to consist of thin fibrous (~10 nm) network. In addition the gel morphology was found to be chemo-responsive and could be extensively modulated by B18-C-6 and K\(^+\) ions. The responsive nature of the gel also provided valuable insights into the key molecular interactions which might be helpful in rationalizing the course of aggregation. These gels are currently being further investigated to explain the role of the mercury(II) cation in the gelation process and to elucidate the exact mode of self-assembly.

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**Notes and references**

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