COMMUNICATION

Transition metal ion induced hydrogelation by amino-terpyridine ligands†

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Hydrogelation behavior of two amino-terpyridine ligands in the presence of divalent metal ions in water was studied in detail. The effect of ligand structure and different counter anions on the gel morphologies was also explored.

In the past few decades, there has been great interest in elucidating mechanisms responsible for self-assembly of small molecules into hierarchical nanostructures. Supramolecular gelators have attracted particular attention because of the expanding usage of gels in fields such as optoelectronics,[1] medicines,[2] organic–inorganic hybrid materials[3] *etc.* Although, most commercial gels are polymeric in nature,[4] one great advantage of supramolecular gels lies in the dynamic nature of the assemblies which allow structural modulations at the molecular level. Several such functional materials have been reported in recent literature where the physical properties of the material could be modified by applying external stimuli[5] such as pH,[6] light,[7] chemical agents[8] *etc.*, thus greatly expanding the scope of such systems for target oriented applications. Among various chemical stimuli applied to modify gel behavior, cations and anions have been the most common regulators.[9–12] In cases of hydrogelators with metal binding motifs, introduction of metal ions in water was shown to have profound effects on the self-assembly process. In many of the metallogels, the formation of the 3D gel network was found to be solely dependent on the presence of a particular metal ion.[13–15] Also, in some cases, gelators have been deliberately designed to have metal-binding motifs to enhance selectivity.[16]

Terpyridines have been extensively used to complex transition metal ions and have often served as building blocks for larger macromolecular structures.[17] However, due to low solubility in water, very few studies exist about their self-assembling properties in aqueous media.[9,18,19]

Recently, we discovered selective gelation behavior of an amino-terpyridine ligand upon binding Hg(II) ion. The results were particularly intriguing considering the lack of any specific Hg(II) binding motif on the gelator.[20] When analogues terpyridines were studied in details for clues regarding metal induced gelation, identity of metal ions as well as subtle changes in the ligand structure was found to have critical impact on the overall gelation process. In certain cases these gels have interesting properties such as pyrophosphate detection at nanomolar concentrations.[21]

Herein we report interesting gelation behaviors of 4′-(4-*N,N*-dimethylaminophenyl)-2,2′:6′,2″-terpyridine (**L1**) and 4′-(4-aminophenyl)-2,2′:6′,2″-terpyridine (**L2**) (Scheme 1) in presence of divalent transition metal ions and how small changes in the gelator molecule led to significant changes in the self-assembly process.

Ligand **L1** was synthesized following a literature method.[22] Ligand **L2** was synthesized by the Suzuki cross-coupling reaction between 4′-chloro-2,2′:6′,2″-terpyridine and 4-aminophenylboronic acid pinacol ester in dimethoxyethane solvent in the presence of Na_2CO_3 using $Pd(PPh_3)_4$ as catalyst (Scheme 2).

Uniform conditions were used for gelation experiments with both the ligands. **L1** and **L2** were solubilized in an aqueous solution of 0.15 N HCl. At this pH, electrostatic interactions between partially protonated ligands and water were too strong to allow self-assembly and resulted in clear solutions. However, as observed previously,[20,21] metal coordination

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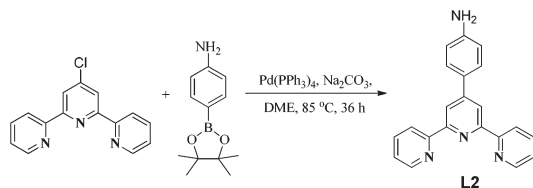
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Scheme 1 Chemical structures of the terpyridine ligands **L1** and **L2**.

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Scheme 2 Synthesis of ligand **L2**.

Table 1 Gelation studies of **L1** and **L2** (8 mM) with different divalent metal (8 mM) ions (S = solution, P = precipitate, G = gel)

Ligand	Mg(II)	Ca(II)	Mn(II)	Fe(II)	Ni(II)	Co(II)	Cu(II)	Zn(II)	Cd(II)	Hg(II)
L1	S	S	P	P	P	P	G	G	G	P
L2	S	S	P	P	P	P	P	G	G	G

significantly altered solubility and charge polarization in the complexes, leading to self-assembly and eventual gelation. Several divalent metal ions were screened for the ability to induce gelation (Table 1).

Although, most of the metal ions caused precipitation of the resulting complexes, it was found that addition of Zn(II)[21] and Cd(II) to both ligands led to gelation. More interesting results were observed for Cu(II) and Hg(II) cations. Cu(II) was found to induce gelation upon complexation with **L1** but not with **L2**, whereas Hg(II) showed the exact reverse behavior (Fig. 1). This was quite intriguing considering only minor structural differences exist between the two ligands.

The metal to ligand ratio was optimized to 1 : 1 for all the gelation experiments. It was observed that the acidic environment and hence the protonation of the amino terminal was crucial for gel formation. It can also be assumed that π–π stacking interactions as well as the salt bridge interactions would play a major role in the self-assembly of the complexes. However the properties of the metal ion that differentiate between precipitation and gelation are not absolutely clear at this point. Although the trends for both the ligands suggested that gelation is favored in case of larger cations where hydration is weak enough to allow other interactions. During the course of our investigation, all the gels formed were found to be thermo-irreversible and thixotropic.

To better understand the nucleation and propagation of the self-assembly in different cases, the gel morphology was
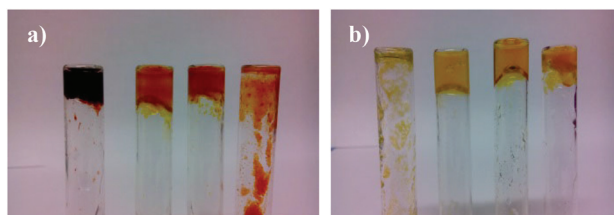

Fig. 2 SEM images of xerogels of (a) Zn(II):**L1**, (b) Zn(II):**L2**, (e) Cd(II):**L1** and (f) Cd(II):**L2**; TEM images of xerogels of (c) Zn(II):**L1**, (d) Zn(II):**L2**, (g) Cd(II):**L1** and (h) Cd(II):**L2**.

elucidated by SEM (scanning electron microscopy) and TEM (transmission electron microscopy) techniques. Although all gel networks mostly comprised of thin fibers, distinct structural differences were observed in case of each metal ion. Significant morphological variations were also observed between the two ligands **L1** and **L2** for the same metal ion (Fig. 2).

The dried Zn(II) hydrogels (xerogels) with both **L1** and **L2** showed uniform fibrous morphology in both SEM and TEM. While TEM images of the gels in both cases revealed dense network of thin fibers (~50 nm width), presence of larger aggregates (formed by higher order assemblies of smaller fibers) were discovered through SEM analysis. However, distinct structural differences were obtained in case of Cd(II) gels. While Cd(II) gel of **L1** showed typical fibrous structure (~80–100 nm width), both SEM and TEM analysis showed Cd(II):**L2** xerogel to be consisting of unusual flake like aggregates (small flat fibers of 120–150 nm width).

Fig. 1 Hydrogels of (a) **L1** with Cu(II), Zn(II), Cd(II) and (precipitate with) Hg(II) (left to right); (b) **L2** with Cu(II) (precipitate), Zn(II), Cd(II) and Hg(II) (left to right).

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Both Cu(II):**L1** and Hg(II):**L2** gels also have fibrous morphology. However the fibers were found to be much thinner in case of Cu(II):**L1** gel than Hg(II):**L2** gel (see ESI† for SEM and TEM images).

To better understand the structural anomalies and varying nature of interactions responsible for such behavior, crystal structures of the parent complexes were analyzed in detail. Due to extreme difficulty in obtaining the single crystals under exactly the same conditions which led to the gelation, the corresponding hydrogels were dissolved in DMF and slowly evaporated to afford single crystals of the coordination complexes CuCl$_2$(**L1**), ZnCl$_2$(**L1**),[21] CdCl$_2$(**L1**), ZnCl$_2$(**L2**), CdCl$_2$(**L2**) and HgCl$_2$(**L2**). The crystal structures confirmed the formation of 1 : 1 complexes in which the metal centers adopt distorted trigonal bipyramidal N$_3$Cl$_2$ coordination. Fig. 3a shows the crystal structure of CdCl$_2$(**L1**), while structure of CdCl$_2$(**L2**) is depicted in Fig. 3b.

Although the coordination geometry around the metal centers in all the complexes is identical, some minor differences were observed when comparing the structures of the
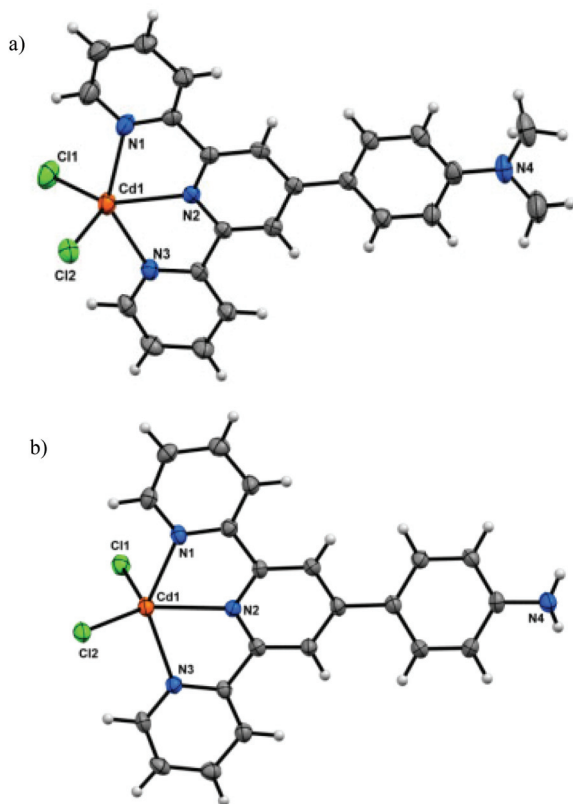

Fig. 4 Crystal packing of ZnCl$_2$(**L2**) showing π⋯π (yellow dotted bond) and N–H⋯Cl interactions (red dotted bond) (top) and the dimeric motif in the crystal packing of CuCl$_2$(**L1**) showing π⋯π interactions (bottom).

Fig. 3   (a) ORTEP plot of the molecular structure of CdCl$_2$(**L1**). Selected bond distances (Å) and angles (°): Cd(1)–N(1) 2.371(4), Cd(1)–N(2) 2.302(3), Cd(1)–N(3) 2.353(4), Cd(1)–Cl(1) 2.4202(14), Cd(1)–Cl(2) 2.4548(13), Cl(1)–Cd(1)–Cl(2) 114.16(5), N(2)–Cd(1)–N(1) 69.14(13), N(2)–Cd(1)–N(3) 69.64(13); (b) ORTEP plot of the molecular structure of CdCl$_2$(**L2**). Selected bond distances (Å) and angles (°): Cd(1)–N(1) 2.341(2), Cd(1)–N(2) 2.299(2), Cd(1)–N(3) 2.350(2), Cd(1)–Cl(1) 2.4762(8), Cd(1)–Cl(2) 2.4238(8), Cl(1)–Cd(1)–Cl(2) 119.76(3), N(2)–Cd(1)–N(1) 69.75(9), N(2)–Cd(1)–N(3) 70.40(8). Thermal ellipsoids are shown at 50% probability level.
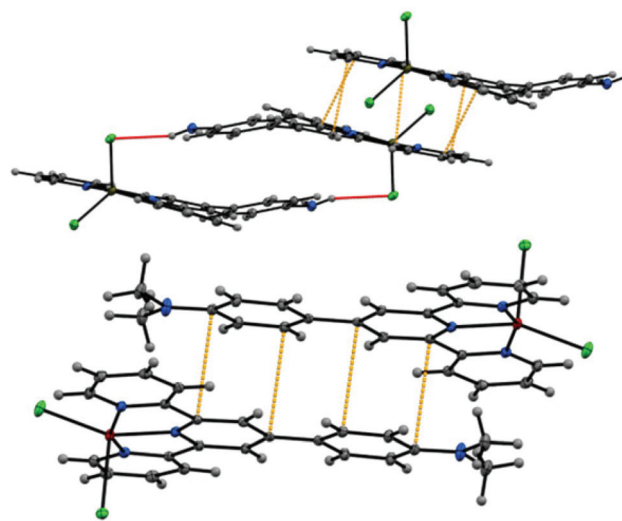
complexes. While the ligand **L1** was found to be planar in all the three complexes, the aniline moiety of ligand **L2** in each of the three complexes was found to be distorted from the planarity. Analysis of crystal packing of metal complexes of **L2** revealed the presence of π⋯π interactions between the terpyridine domain of the neighboring complexes as well as N–H⋯Cl interactions (between the terminal Cl atom and adjacent anilinic H-atoms) (Fig. 4). However, the crystal packing of metal complexes of **L1** was mainly governed by π⋯π interactions (Fig. 4).

The evidence from the crystal packing of the complexes suggested that the weak interactions such as π⋯π interactions between neighboring complexes might play an important role in the self-assembly. In addition, the N–H⋯Cl interactions have also influenced the self-assembly of **L2** complexes. Anions were found to have a profound effect on gelation process, especially in cases where metal coordination is involved.[23] Dong *et al.* recently demonstrated that the fiber dimensions can be regulated by Cl$^-$ ions controlling the charge distribution on π-conjugated molecules.[24] This prompted us to investigate the effect of anions on the gelation process. For this purpose, the gelation experiments were repeated by dissolving ligands **L1** and **L2** in 0.15 N of different acids (only strong acids were selected to ensure complete dissociation and to maintain constant counter anion concentrations[25]). Gelation occurred uninterrupted with Zn(II), Cd(II) and Hg(II) complexes irrespective of the counter anion present.[25] However, in case of Cu(II), gelation (with ligand **L1**) was found to be critically influenced by the presence of anions and only happened in the presence of HCl and HBr (Fig. 5).

To investigate the role of anions further, the following study was conducted. Addition of 1 equivalent of Cu(ClO$_4$)$_2$ to **L1** (dissolved individually in 0.15 N of HNO$_3$, H$_2$SO$_4$, HBr, HClO$_4$ and *p*-toluenesulfonic acid) in presence of 1 equivalent
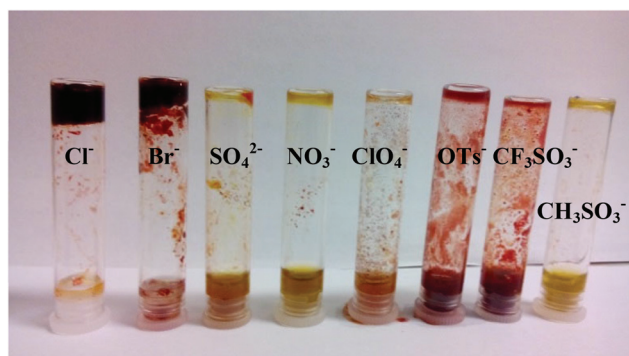
Fig. 5 Cu(II):**L1** (8 mM/8 mM) system after dissolving **L1** in HCl, HBr, H_2SO_4, HNO_3, $HClO_4$, p-toluenesulfonic acid, CF_3SO_3H and CH_3SO_3H (left to right).
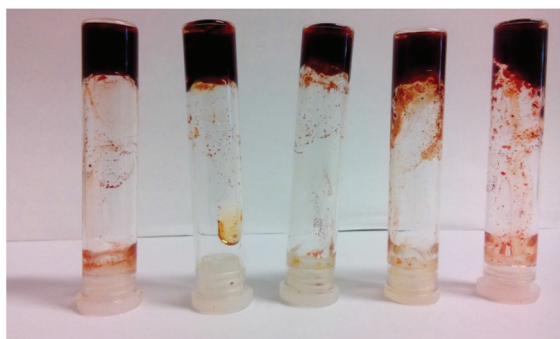

Fig. 6 Cu(II):**L1** (8 mM/8 mM) Gels in presence of 8 mM NaCl after dissolving **L1** in HNO_3, H_2SO_4, HBr, $HClO_4$ and p-toluenesulfonic acid (left to right).

of Cl^- (NaCl), always led to gelation irrespective of the large excess of other counter anions in the system (Fig. 6).

The results confirmed the importance of Cl^- ion in the gelation process. Although the reason for this interesting gelation behavior is not well understood, the smaller size of Cu(II) ion and hence stronger polarisability might have a critical impact on the self-assembly.

In conclusion, the self-assembly behavior of divalent metal complexes of two simple amino-terpyridine ligands **L1** and **L2** in water was explored in detail. It was observed that hydrogelation depended critically on the metal ions and also on minor changes in the ligand structure. The crystal packing of both the ligand-complexes showed definite differences that might have led to the morphological changes in the corresponding gel structures. The observation of the role of the metal ion in controlling the dimensions of such aggregated structures was intriguing. Given that the terpyridine based gelators were not explored until recently, this study could provide valuable insights into the dynamics of such system and would help creating new class of metal ion responsive materials.

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