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Homochiral coordination polymeric gel: Zn^{2+}-induced conformational changes leading to J-aggregated helical fibres formation†

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A novel chiral coordination polymeric gel based on an amino acid derived symmetrical ligand, specific base, and Zn^{2+} has been described. Zn^{2+} induced conformational reorganization in the ligand leads to gelation *via* J-aggregated helical fibres. The vital role played by π–π stacking in gelation has been monitored by fluorescence and NMR spectroscopy.

Gels have attracted immense current interest because of their potential application in diverse areas.[1] The majority of gelators are long chain amphiphiles based on amino acids,[2] sugars,[3] and pyridine[4a] possessing amide head groups. Usually the gelators form a hydrogel or organogel alone or together with neutral organic molecules as additives.[4b] Further, organic hydro-organogels have been more extensively investigated relative to metal–organic gels; metallogelators[5a,b] or coordination polymers.[5c] Essentially, there is no obvious difference between an organogelator and a metal–organic gel. However, the incorporation of a metal centre, particularly a transition metal, influences the self-aggregation modes and allows additional scope for tuning the gel properties.[1b,5]

Coordination-based gels may be associated with additional physicochemical properties such as magnetism, colour, rheology, adsorption, emission, catalytic activity and redox behaviour.[5] Recently, Vittal *et al.*, reported a chiral coordination polymeric (CP) gel based on a glycine derived ligand and Zn^{2+} which displayed enormous fluorescence enhancement.[6] In addition, chiral gelators have attracted immense interest because gelation often leads to helical twisting of the fibres,[7] inducing chiro-optical effects.[5d] Though there are few reports on the conformational change pertaining to helix formation involving organic derivatives,[8,9a] such an observation has not been made with coordination polymeric gels.

Considering these points, through this contribution we describe homochiral coordination polymeric gel based on L-tyrosine derived ligand **1** ($H_4T^{L\text{-tyr}}$), KOH and Zn^{2+}. Herein, metal coordination not only influences conformational changes in the ligand but, also induces gelation accompanied by J-aggregated helical fibre formation and remarkable fluorescence enhancement. The Zn^{2+} induced conformational reorganization in the ligand **1** leading to gelation has been monitored by fluorescence, CD, and NMR spectroscopy.[9b] Moreover, the twisted helical fibrous morphology has been revealed by AFM.

The ligands **1–3** were synthesized in good yield and characterization data are consistent with proposed formulations (Scheme S1, ESI†). Addition of a methanolic solution of $Zn(NO_3)_2{\cdot}6H_2O$ to a deprotonated solution (using KOH or NaOH) of **1** forms CP gel **4** (0.9%, w/v) instantly at room temperature, which was confirmed by the inverted test tube method (Fig. 1). The CP complex **4** was well characterized by elemental analysis, IR, ESI-mass spectrometry and TGA. In addition, **1** can also be gelated using various zinc counter ions such as Cl^-, ClO_4^- and OAc^- indicating that the CP gel formation with **1** does not strongly depend on the nature of the anion. Interestingly, gelation was

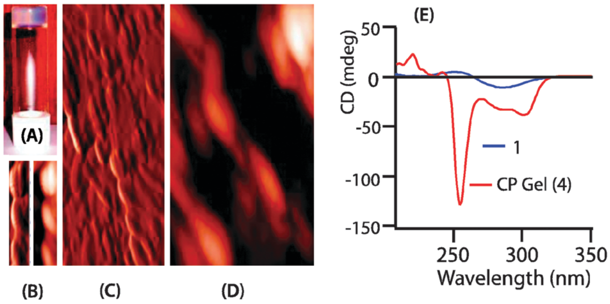

Fig. 1 (A) Photograph of the CP gel **4** in an inverted vial, (B) AFM image showing single helical twisted fibres, (C) phase mode image, (D) magnified image of two twisted helical fibres intertwined with each other and (E) CD spectra for **1** (blue line) and diluted CP gel **4** (red line).

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not observed in other common organic solvents or in presence of the metal ions including Co^{2+}, Ni^{2+} and Cu^{2+}. Furthermore, deprotonation of **1** with $LiOH{\cdot}H_2O$ could not lead to gel formation. The loss of gelation was also observed when the hydrophobic polar arm of **1** (L-tyrosine) was replaced by other hydrophobic non polar amino acids like L-leucine or L-phenylalanine. In fact, ligand **2** and **3** afforded precipitate and gelatinous precipitate respectively, indicating that a small change in gelator could affect the gelation properties. All the isolated complexes were insoluble in water and common organic solvents. The CP gel **4** shows thermo-reversibility which is an uncommon property for coordination polymer gel systems.[6]

Lucid twisted helical fibrous morphology was revealed by AFM (Fig. 1 and Fig. S2–S4, ESI†). The formation of helical fibres is most likely due to the helical arrangement of molecules within the assembly which is supported by the crystal structure of three dimensional CP Cu(II) complex **6** (Fig. S14–S16, ESI†). The structural similarities of **4** and **6** have been thoroughly established by elemental analyses, ESI-MS and TGA. The CD spectra of **1** in methanol (1×10^{-5} M) shows a bisignated Cotton effect, that is negative at lower (λ_{max} = 280 nm) and positive at higher energy (λ_{max} = 252 nm) along with a zero crossing at 265 nm (Fig. 1). On the other hand, diluted CP gel **4** (2×10^{-5} M) shows intense CD signals (λ_{max} = 303, 280 and 252 nm) with a negative Cotton effect. Enhancement of the signal intensity at 252 nm with a negative Cotton effect indicates that chirality transfer becomes more effective with the growth of π–π stacking of the phenolic units. The solid state CD signal of the xerogel also shows a negative Cotton effect (Fig. S10, ESI†). The CD signal transformation at 252 nm supported conformational reorganization of **1** in a helical supramolecular structure upon metal coordination.[7b,9]

The fluorescence spectrum of **1** (1×10^{-4} M, deprotonated with KOH) displayed a broad band with an emission maximum at 306 nm (λ_{ex} = 280 nm, Stokes shift = 26 nm) corresponding to a π–π* transition. Aliquot addition of Zn^{2+} to a methanolic solution of **1** led to a gradual decrease in the intensity of the band at 306 nm and appearance of a new band at 338 nm (Stokes shift = 58 nm) along with an isoemissive point at 315 nm (Fig. S5, ESI†). Notably, the π–π* emission band exhibited a red shift of ~32 nm which may be due to π–π stacking between phenolic rings like excimer formation.[10] This unique red shift upon addition of the Zn^{2+} indicates J-type aggregation which was further attested by UV-vis spectral studies (Fig. S10, ESI†).[11] The remarkable fluorescence enhancement arising from π–π stacking and various hydrogen bonds created by CH_3OH, N–H donor groups and O atoms as hydrogen bond acceptors can be ascribed to the aggregation induced enhanced emission (AIEE) effect.[12] The critical role of phenolic –OH in aggregation towards gelation cannot be ruled out. Such packing can easily be extended to form a CP gel by accommodating methanol molecules tightly in the interstitial solvophilic pockets, together with hydrogen bond donors and acceptors. The crystal lattice of 3D CP **6** further supports the above observation (Fig. S15, ESI†). Job's plot signifies complex formation between **1** and Zn^{2+} in 1 : 1 ratio (Fig. S10, ESI†). On the other hand, when **1** was deprotonated using $LiOH{\cdot}H_2O$, complex formation occurs by the same phenomenon however, the AIEE was not observed and has been supported by comparative fluorescence studies using K^+ and Li^+ (Fig. S5 and S6, ESI†). The IR spectra of **5** shows a shift in the ν_{as}(COO) (~12 cm^{-1}) band relative to **4** which clearly indicates the $>C{=}O{\cdots}Li^+$ interaction. The Li^+ interaction probably interrupts gelation and forms the sol. The effect of alkali metal ions on gel[13a] or self-assembly processes using amino acid derivatives has already been investigated.[13b] Fluorescence emission studies were performed to follow the effect of other metal ions on aggregation behaviour. Neither gel formation nor aggregation occurs in the presence of Co^{2+}, Ni^{2+} and Cu^{2+} ions. Further, gradual and controlled addition of the aforesaid metal ions leads to quenching of the emission band at 306 without any appreciable shift (Fig. S8, ESI†). The non-attendant red shift in the presence of the said metal ions may be attributed to the involvement of the phenol as a fifth axial ligand, in turn, segregation of the π–π stacking. Therefore, it may be concluded that selective Zn^{2+} coordination to **1** enforces conformational changes and thereby aggregation.

The thermo-reversible nature of CP gel **4** was established by variable temperature fluorescence studies. Upon heating up to 64 °C, it illustrated gradual quenching and returns after cooling to 20 °C (Fig. S9, ESI†). The band due to π–π* exhibited substantial blue shift (~32 nm) with a huge drop off in intensity (~70%) upon addition of dilute HCl to the CP gel **4** (Fig. S5, ESI†). It suggested disruption of the gel into sol and may be attributed to protonation of the ligand at low pH, thereby blocking the coordination sites and, in turn altering the aggregation pattern of the gel.

In the ^{1}H NMR spectrum, phenolic protons of the free ligand **1** displayed broadening and significant downfield shift ($\Delta\delta$ = 0.2 and 0.1 ppm) upon addition of Zn^{2+} (1 equiv.). It supported the occurrence of π–π stacking between phenolic rings (Fig. S11, ESI†). Further, the aromatic ring (~7.18 ppm) as well as aliphatic protons did not show any significant shift except broadening of the respective signals which strongly supported the aggregation involving phenolic ring (π–π) stacking.[14] In the case of Cu^{2+}, no significant shifts for any protons were observed which eliminates the possibility of π–π stacking and axial coordination of the phenolic groups. It is consistent with the observations made from fluorescence titration studies (Fig. S8 and S11, ESI†). This also supports that π–π stacking between phenolic rings plays a role in the gelation process. In addition, a conformational change in the ligand **1** upon coordination with the metal has been affirmed by geometry optimizations and its crystal structure (Fig. S17, ESI†). Based on morphology, results from spectral and structural studies we summarize results for CP gel formation in Fig. S18 (ESI†).

A gel must show specific rheology *viz.* mechanical or elastic strength. The mechanical strength of a gel is measured by its storage modulus (G') and loss modulus (G'') which depend on the gelator concentration. The rheological experiments have been performed using freshly prepared CP gel **4** at fixed concentration (0.9%, w/v). The storage modulus G' and loss modulus G'' were measured as a function of shear stress at 20 °C, at a frequency of 1 rad s^{-1}. From the available data it is clear that initially G' is higher relative to G'' by 1 order of magnitude and maintained the

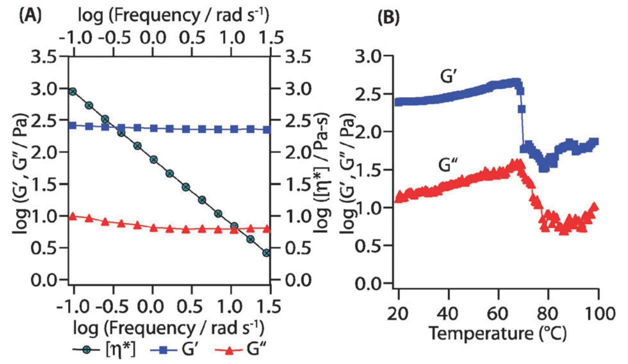

Fig. 2 (A) Primary axis: dynamic frequency sweep measurements of G' and G'' for CP gel **4**, at strain of 0.5%. Secondary axis: complex viscosity measurements. (B) Dynamic temperature ramp G' and G'' for CP gel **4** at a heating rate of 1 °C min^{-1}, strain of 0.5% and frequency of 1 rad s^{-1}.

difference over a large range of shear stress (Fig. S13, ESI†). This is an indispensable behaviour expected for a true gel phase.[15] With a gradual increase in the applied stress both G' and G'' remain almost invariant (linear viscoelastic region) and at a certain yield stress ($\sim$8 Pa), these cross each other indicating mechanical break-up of the gel and beyond yield stress these deviate from linearity and follow the gel–sol phase transition. The frequency sweep (Fig. 2) measurements indicate that G' and G'' values of the CP gel **4** are independent of the frequency (f) at any given frequency in the experimental frequency region (−1.0–1.5 rad s^{-1}); the G' is greater than G'', suggesting that CP gel **4** behaves as a gel phase material. The double logarithmic plot of complex viscosity η^* *vs.* angular frequency ω having a gradient close to −1, implies constant declination of the viscosity with increasing frequency.

The storage modulus (G') and loss modulus (G'') have been measured in the range 20–100 °C. For a gel phase material G' should be higher than G'' and $G' < G''$ when the gel starts to break into the sol. This criterion is adequately followed by our gel system in the said temperature range. At 67 °C, an abrupt change was recorded in storage modulus and loss modulus which indicated deformation of the CP gel (Fig. 2). A pointed change found in the loss tangent ($\tan\delta = G''/G'$) at 67 °C indicates the critical temperature (T_{gel}) for CP gel. Overall, the phase transition occurs *via* gel–semi sol–solid, which is expected for CP gel (methanolic) (Fig. S13, ESI†) and suggests the formation of a typical 'soft-solid like' gel phase material.[16] It is consistent with the observations made from variable temperature fluorescence studies.

In conclusion, through this work we have described a unique class of thermo-reversible, chiral coordination polymer gel based on an L-tyrosine derived symmetrical ligand, KOH and Zn^{2+} where metal coordination induces conformational changes in ligand, which causes J-aggregated helical fibre formation with dramatic fluorescence enhancement. The J-aggregation and fluorescence intensity enhancement is mainly due to the π–π stacking interaction between phenolic rings. Moreover, AFM and CD analysis provided evidence of the formation of twisted helical fibres. Rheological studies revealed phase transition *via* gel–semi sol–solid at T_{gel} and gel–sol at yield stress. The present gel may find applications in chiro-optical, optoelectronic devices and also **1** can be used for sensing metal cations.

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