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Are Gelation behaviour Predictable through Crystal Engineering Approach? A Case Study in Four Similar Coordination Compounds

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CORRESPONDING AUTHOR FOOTNOTE: Hamid Reza Khavasi, Tel No: +98 21 29903105, Fax No: +98 21 22431661. In the present paper, a detailed study on the gelating properties of a series of terpyridine and dipyrazine-pyridine ligands in the presence of metal salts has been reported. In order to reveal driving forces for the self-assembling of the metallogelators, their crystal structure has been scrutinized. Inspired by the gelation of CuCl₂[Terpy-nCN], where "Terpy-nCN " is 4'-(ncyanophenyl)-2.2',6',2"-terpyridine, in order to look into the aggregation behaviour of the related analogues, synthesizing CuCl₂[Dipyz-py-nCN] derivatives, where "Dipyz-py-nCN " is 4-(ncyanophenyl)-2,6-di-pyrazin-2-yl-pyridine, with the same cyano groups was performed. We then found that the Dipyz-py counterpart forms crystal when the molecules are stacked in an alternating way, instead of unidirectional one requested in gel formation. Crystal engineering approach was applied to determine the interactions that are favourable for fabricating a fiber network that is likely to be present in both crystalline and gel state and founding the interaction that disturbs this delicate balance between gelation and crystallization in coordination compound, then we concluded that the subtle balance of molecular shape and intermolecular interactions are what the gelation and crystallization of the current molecular system are obtained from. This enables us to find the mutual connection between the structure of molecules, assembly behaviour as well as intermolecular interactions. With our experiments, a deep understanding of the balance between the solution, gelation and crystallization with subtle molecular diversions was provided.

Introduction

Since not long ago, having a high potential for a wide range of advanced applications, molecular gels have evolved as a fascinating class of materials.¹⁻²¹ Despite intense research on these materials, lack of design rules is probably the main issue that hindered forming gels by linking molecular structure to the ability of a molecule. Even so, there are reports indicating that molecules that are highly similar to each other in term of their structure, actually, show very different abilities when forming a gel^{22-24} . In these studies, libraries of molecules were formed by changing the molecular structures. Although the reason behind this phenomenon is not very clear, it may be due to the self-assembly resulting to gelation levitates from a fine balance of non-covalent interactions. Hence, a slight modification of intermolecular interaction of can turn a gelator into becoming a non-gelator²⁵. As of now many interesting results have been gained but the most successful method for creating new gelators is believed to be modifying known gelator scaffolds^{26–28}Despite the fact that great attempts are still allocated to the investigation of the subtle structural demands and molecular motifs that control the behaviour of a given compound, the features for a certain molecule to act as a gelator have remained as a significant challenge. There is a hypothesis that suggests to build up macromolecule-like aggregates, having intermolecular interactions is an important criterion for developing gelators. It can be concluded that before unidirectional (or 1D) interactions lead to the fiber-like morphologies they should promote 1D self-assembly first²⁹⁻³³. These fiber-like morphologies are typically observed in molecular gels. Their strong propensity to self-assemble unidirectionally through a set of noncovalent bonds is what differentiate systems like this from others. Simultaneously, this network of interactions must not make the system to be too ordered that ends up to precipitation/crystallization³⁴. The dynamic nature of gel systems aggravates the complexity of

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such a picture, which exhibits anisotropically reversible sol-gel transition upon exposure to external physical or chemical stimuli at most of the times. However, a drawback of many supramolecular gels is that they have a great propensity to crystallize over time. This phenomenon leads to the gel collapsing and limits its lifetime stability³⁵⁻³⁷. Crystal formation of a supramolecular gel is based on this fact that the gel is a metastable phase ^{23,35}. Over time, gelator molecules assemble to generate nucleation points, decreasing the available gelator concentration, which can cause crystallization^{38,39}. Such phenomena decrease the gel lifetime and therefore its usefulness. So, developing platforms to avoid small molecule supramolecular gelator crystallization has gained the interest of many⁴⁰. To this end, several design strategies have been proposed, original work in designing long-lived supramolecular gels revolved around the design of the gelator itself. These strategies are based on criteria to achieve supramolecular gelating apparent in the process, first by the presence of unidirectional interactions and robust selfcomplimentary to enforce one-dimensional self-assembly, and after that by the control over the fiber-fiber interfacial interaction to control 3D network formation and to prevent crystallization. To design these gelators including pincer type ligands, some supramolecular synthon approaches are employed; (a) straightforward method including the identification of molecular scaffolds that show predominant 1D intermolecular interactions in the solid-state, (b) the aggregation resulted from the unidirectional stacking of molecules to fabricate fiber like networks, (c) attaching functional groups with directional interactions. To create new gelators, the cyano groups have been successfully used. In terms of directionality, cyano group has multiple forms of interactions. Using robust supramolecular synthon which leads to one-dimensional self-assembly of terpyridine derivatives with cyano group, producing stable and crystallization-free gels. So, our interests next turned to investigate the potential strategies to tune the properties of

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supramolecular gels, albeit, systematically which results in enhancing the lifespan stability of terpyridine-based hydrogels gel up to a noticeable point. A number of functionalized terpyridines have shown to be efficient gelators⁴¹⁻⁵⁰.

Standing as an adoptable family of molecules that have been formerly employed in the study of gel formation successfully, terpyridine compounds include terpyridine, which is functionalized at the central ring with an aromatic group, electron withdrawing group, donating group or heterocyclic substitution such as furan, thiophene, oxazole and etc⁵¹⁻⁵⁷. Here, a complete survey on the gelating properties of a series of terpyridine and dipyrazine-pyridine ligands, CuCl₂[Terpy-nCN] and CuCl₂[Dipyz-py-nCN], [Terpy-nCN] is 4'-(n-cyanophenyl)-2,2',6',2''terpyridine, and [Dipyz-py-nCN], is 4-(n-cyanophenyl)-2,6-di-pyrazin-2-yl-pyridine, Scheme 1, in the presence of metal salts is reported. In general, establishing H-bonding interactions, $\pi - \pi$ stacking contacts and metal coordination by using simple and usually available ligands like this is doable. In our studies on a series of CN-substituted terpyridine ligands and their dipyrazinepyridine counterparts, we observed that very subtle changes in the structure of the molecule, though alteration like this might seem tiny, had an intense effect on the outcome of the assembly process and the ability of the ligands to form the gel. As mentioned earlier, the structures of the molecules and unidirectional interactions has been the main focus of scientists. One noticeable challenge that is still unsolved is addressing the fact that small alterations to the structure of a gelator can unpredictably lead to the disruption of the formation of the gel. Specifically here, we will talk about the assembling process of two copper complexes including CN-functionalized pincer ligands, CuCl₂[Terpy-4CN], and CuCl₂[Dipyz-py-4CN]. Notice that these complexes are closely related to each other and they only differ only in two nitrogen atoms. As discussed above, these complexes tend to self-assemble themselves and, in turn, form gels. Here, we try the

underlying principles and rules responsible for the phenomenon will be described. Our attention will mainly be on the possible formation of metallogels in terms of the connection between the nature of the gelled component, the designed structure of the gelator and the influence of molecular interactions such as Van der Waals interactions, π - π stacking and hydrogen bonding.

Materials and methods

General. Starting materials and solvents were purchased from commercial sources and used as received. Infrared spectra (4000–250 cm⁻¹) of the solid sample were recorded on a BOMEM-MB102 spectrometer as 1% dispersion in CsI pellets. With the help of a Heraeus CHN-O Rapid analyzer Elemental analysis was performed. A Bamstead Electrothermal type 9200 melting point apparatus was used which provided us to analyze melting points.

Synthesis of ligands [Terpy-3CN] and [Terpy-4CN]. Ligands [Terpy-3CN] and [Terpy-4CN], differ only in the substitution position of CN group in terpyridine ligands. The synthesis of both compounds is relatively straightforward. They are conveniently prepared in a one pot synthesis procedure according to methods described previously⁵⁸. 4.84 gr (40.0 mmol) amount of 2-acetylpyridine was added into an ethanolic solution (100 mL) of 2.12 gr (20.0 mmol) of 3- or 4-cyanobenzaldehyde. 58 mL (50.0 mmol) of a 29.3% aqueous solution of NH₃ and 3.08 gr (40.0 mmol) of KOH pellets were then added to the reaction solution and then stirred at room temperature for 4 hours. The resulted white precipitate was collected by filtration and then washed three times with 10 mL of ethanol.

For [Terpy-3CN]: yield 65%, m.p=193°C. Anal. Calcd.: C, 79.02; H, 4.22; N, 16.76. Found: C, 78.73; H, 4.53; N, 16.98 FT-IR (cm⁻¹): 3315, 3053, 2235 (v_{C=N}), 1678, 1585 (v_{C=N}), 1471, 1388

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 $(v_{C=C})$, 991, 881,733. ¹H NMR (300 MHz, DMSO-d₆): $\delta = 8.77-8.68$ (6H_{Ar}, m), 8.19 (1H_{Ar}, s), 8.16-8.12 (1H_{Ar}, m), 7.95-7.86 (1H_{Ar}, m), 7.78-7.75 (2H_{Ar},m), 7.68-7.63 (1H_{Ar},s), 7.42-7.38 (2H_{Ar},s). ; ¹³C NMR (400 MHz, DMSO-d₆): $\delta = 110.93$, 111.16, 118.94, 119.19, 120.82, 121.46, 122.46, 126.91, 127.41, 129.51, 130.26, 132.08, 132.89, 136.63, 137.34, 143.76, 144.08, 147.87, 148.54, 153.86, 154.60, 163.37.

For [Terpy-4CN]: yield 73%, m.p=198°C. Anal. Calcd.: C, 79.02; H, 4.22; N, 16.76. Found: C, 79.45; H, 4.02; N, 16.81. FT-IR (cm⁻¹): 3334, 2224 ($\nu_{C=N}$), 1680, 1585 ($\nu_{C=N}$), 1469, 1388 ($\nu_{C=C}$), 1074, 993, 835, 787, 731. ¹H NMR (300 MHz, DMSO-d₆): $\delta = 8.77$ (1H_{Ar}, d,J=3.0Hz), 8.72 (1H_{Ar}, s), 8.67 (1H_{Ar}, d, J = 6.0 Hz), 8.14-8.13 (1H_{Ar}, m), 8.11-8.02 (2H_{Ar},m), 7.55-7.52 (1H_{Ar},s). ; ¹³C NMR (400 MHz, DMSO-d₆): $\delta = 156.4$, 155.1, 149.9, 148.3, 142.5, 142.5, 138.0, 133.7, 128.5, 125.2, 121.5, 118.7 and 112.4.

Synthesis of ligands [Dipyz-py-3CN] and [Dipyz-py-4CN]. For [Dipyz-py-3CN], and [Dipyz-py-4CN], the synthetic method was similar to that of terpyridine ligands, except starting material 2-acetylpyrazine was used instead of 2-Acetylpyridine.

For [Dipyz-py-3CN]: yield 81%, m.p=258°C. Anal. Calcd.: C, 71.42; H, 3.60; N, 24.99. Found: C, 71.18; H, 3.83; N, 24.83. FT-IR (cm⁻¹): 3367, 3051, 2233 ($v_{C=N}$), 1678, 1603 ($v_{C=N}$), 1471, 1369 ($v_{C=C}$), 1120, 1018, 854, 810, 688.

For [Terpy-4CN]: yield 75%, m.p=250°C. Anal. Calcd.: C, 71.42; H, 3.60; N, 24.99. Found: C, 71.63; H, 3.85; N, 24.78. FT-IR (cm⁻¹): 3043, 2225 ($\upsilon_{C=N}$), 1680, 1604 ($\upsilon_{C=N}$), 1471, 1375 ($\upsilon_{C=C}$), 1111, 1018, 835, 789.

Synthesis of pincer-type Cu(II) Complexes: All complexes were prepared by following synthetic methodology. A solution of 10 mmol of ligand in 5 mL methanol was added to a

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solution of 10 mmol of copper(II)chloride in 5 mL methanol and then heated at 50 °C for 5 min. Green precipitate was collected by filtration and purified by recrystallization in methanol.

For CuCl₂[Terpy-3CN]: yield 63% based on the copper salt, m.p=decomposed at 176°C. Anal. Calcd.: C, 56.36; H, 3.01; N, 11.95. Found: C, 56.68; H, 3.22; N, 12.25. FT-IR (cm⁻¹): 3354, 3049, 2231 ($\nu_{C=N}$), 1583 ($\nu_{C=N}$), 1402 ($\nu_{C=C}$), 1020, 795.

For CuCl₂[Terpy-4CN]: yield 75% based on the copper salt, m.p=above 270°C. Anal. Calcd.: C, 56.36; H, 3.01; N, 11.95. Found: C, 56.42; H, 3.25; N, 11.73. FT-IR (cm⁻¹): 3427, 3049, 2225 ($v_{C=N}$), 1603 ($v_{C=N}$), 1469 ($v_{C=C}$), 1248, 1016, 837, 793.

For CuCl₂[Dipyz-py-3CN]: yield 81% based on the copper salt, m.p=decomposed at 260°C. Anal. Calcd.: C, 51.02; H, 2.57; N, 17.85. Found: C, 51.16; H, 2.73; N, 17.93. FT-IR (cm⁻¹): 3354, 3052, 2348 ($v_{C=N}$), 1581 ($v_{C=N}$), 1392 ($v_{C=C}$), 1176, 1039, 814.

For CuCl₂[Dipyz-py-4CN]: yield 69% based on the copper salt, m.p=above 270°C. Anal. Calcd.: C, 51.02; H, 2.57; N, 17.85. Found: C, 51.35; H, 2.73; N, 17.26. FT-IR (cm⁻¹): 3360, 3030, 2351 ($\nu_{C=N}$), 1606 ($\nu_{C=N}$), 1400 ($\nu_{C=C}$), 1173, 1039, 854.

Preparation of the Gels: In a typical gelation test a weighed amount of the copper complex containing [Terpy-3CN] or [Terpy-4CN] ligand was mixed with a measured volume of the solvent such as pure water or mixed solvent. The mixture was sonicated for 30 seconds and the heating process was performed until the solid was fully dissolved. The resulting solution was allowed to cool down to room temperature, a more common way to bring about the necessary supersaturated solution from which gel fibre growth is possible is slow cooling. The results were confirmed by the tube inversion test. The minimum gelation concentration (MGC) was determined by scaling a minimum amount of gelator needed for the formation of a stable gel. As for measuring the gel to the sol transition temperature, T_{gel} , the inversion test method was used.

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Notice that, for each sample, we repeated the process three times. The gels were optically transparent with thixotropic properties. In contrast, brief sonication of mixture led to slightly opaque gel that did not flow under tube inversion. Both kinds of gels were quite stable for several months.

Crystallization of Complexes: Despite doing our best, our experiments resulted in the crystallization of the complexes (CuCl₂[Terpy-4CN], CuCl₂[Dipyz-py-3CN] and CuCl₂[Dipyz-py-4CN]), by slow evaporation from a methanol solution. In the case of CuCl₂[Terpy-4CN], when the solvent of slow evaporation changed from MeOH to a mixture of water and MeOH, different kinds of crystals of CuCl₂[Terpy-4CN], were obtained. Single crystal diffraction analysis showed that these two CuCl₂[Terpy-4CN] crystals are pseudo polymorphs.

Results and Discussion

Gelation behaviour: We carried out the gelation test at 1 mg.mL⁻¹ concentration in water. After sonication of the samples for 30 seconds, we slow heated the samples until the solid was completely dissolved. Afterwards, we allowed the sample to cool down to room temperature, Figure 1. Gels formed in water are the strongest and the most optically transparent and stable one. It must be noted that although these pincer ligands were hardly dissolved in water, by addition of CuCl₂ salt (0.1 wt%), in 1:1 molar ratio to ligand, it only took an hour for the white solid of ligands to dissolve during the stirring process *via* coordination to copper ion, Figure 1. A stable gel was formed upon standing for several months. The gel even was formed during the stirring process with a higher gelator concentration of >0.1 wt%. The gel superstructure, if the gel is heated above the gel-to-sol phase transition temperature, actually gets disrupted. This leads to the reformation of the isotropic solution. It is best to be noted that Upon cooling, the sol

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actually reverts back to its former from which is a gel. This reversible process can be repeated for a great number of cycles. In addition, the metallogel transformed into a viscous sol upon shaking and altered into a robust gel again upon resting, which indicated thixotropic behaviour and self-healing abilities of the gels. The gelation ability of gelator was examined in a variety of alcohols and various aqueous media at the critical concentration of gelator listed in Table 1. In contrast to the fact that the formation of many of the gels only occurred within a few minutes, the process of crystallization of some of the samples actually took over an hour. As it is clear from Table 1, the solvent structure is an important factor in the formation of the gels. Focusing on bulk gelator solubility, gelators should not be too soluble or too insoluble in solvent systems. Complexes can only gelate mixed solvents. The reason behind this is that the solubility in most of the chosen pure solvents is actually lower than the mixed ones. In addition, the MGC of complexes in pure water was also researched on; gelator concentration is lower than what we observed in water-miscible organic solvents.

The terpyridine–Cu(II) complexes form gels in H₂O, mixture of H₂O:MeOH (1mL:10mL), H₂O:EtOH (2mL:10mL), H₂O:PrOH (3mL:10mL), H₂O:IsoPrOH (4mL:10mL) and H₂O:Aceton (2mL:1mL), Table 1. Meanwhile, a plot of the gel–sol dissociation temperature, which is the needed temperature for the conversion of gels into liquids (T_{gel}), *versus* the gelator concentration in the various solvent was built. This was for the evaluation of the thermal stability of the Cu(II) metallogels. Figure 2 clearly shows the increasing of T_{gel} as the concentration of the gelator also increases. These indicate that the thermal stability depends on non-covalent interaction ability of the gelators in various solvents. With this, the supramolecular nature of the gels network was explained. In this network non-covalent interactions such as hydrogen bonding and π - π stacking play important roles for gel network formation. As construction principles, tuning cooperations

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of metal and ligand is widely used for the generation of metallosupramolecular architectures. Metallogelators are systems in which hierarchical self-assembly process affect with both the ligand and metal ion exploit as complementary elements⁵⁹. The gelation ability of ligands with different chloride salts of metal ions such as Co(II), Mn(II), Ni(II), Fe(II), Cd(II) and Zn(II) was further analyzed. In our reaction condition, no obvious gelation was observed. The anionselectivity of the gel formation was also examined for other selected Cu(II) salts which are CuBr₂, CuI₂, Cu(NO₃)₂, and Cu(OAc)₂. As the results didn't show any gel formation, it was concluded that counter anions actually play an important role in the assembly of gels. Upon metal complexation of other salts, maybe the 1D network becomes linked intramolecularly, which hinders the formation of fiber networks and consequently gelation. On the other hand, the solubility of other complexes is different so leads to disturbing the balance between the solubility and further aggregation. The 4CN derivatives of terpyridine type complexes proved to be more soluble than their 3CN counterparts in general solvents such as water, methanol and ethanol and did not exhibit a significant difference in gelation behaviour, but 4CN derivatives formed more stable gel than 3CN and had higher T_{gel}. In comparison with the CuCl₂[Terpy-nCN] complex gelators, for the CuCl₂[Dipyz-py-nCN] homologous complexes, no gels were formed in any solvents and these materials turned to the crystalline state immediately. It is possible that the increased electron withdrawing nitrogen atom in CuCl₂[Dipyz-py-nCN] complexes led to selfassembly in the 3D network and hence disfavored gel formation. It revealed that these materials have large tendency to aggregate and crystallize in the 3D network. Despite this, an active surface on which substrate nucleation can happen in such a way that the periodicity of the gel fiber is underlined and transferred to a growing crystal is offered by the local one-dimensional ordering of gel fibers. This is a process of heterogeneous secondary nucleation. Formation of a

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gel in contrast to crystalline materials is governed by a largely unpredictable balance of noncovalent interactions. Perturbation of this balance may lead to the collapse of gel states to precipitate or crystalline species. In our cases when the metallogels were allowed to stand for several days, the gel did not transform into precipitate or crystalline forms. After several days, the gels only removed the solvent to form xerogels that cannot convert into single crystals in situ, so, are called crystallization-free gels. This observation highlights the lack of suitable interaction for secondary nucleation to the 3D network.

Crystallization Behaviour. Monitoring crystal formation under conditions that favour gelation is not very common as there have been efforts made to correlate the mechanistic basis for crystallization and gelation but none were really convincing and were most confusing and unclear^{60,61}. In our studies complexe CuCl₂[Terpy-4CN] and CuCl₂[Terpy-3CN] are soluble in water, but CuCl₂[Terpy-4CN] was hardly soluble in all selected alcohols, and in the case of CuCl₂[Terpy-3CN] was even worse. Gelators have a high solubility in a water-miscible organic solvent, but a low solubility in water. In contrast to similar gelation behaviour, these two ligands have significant differences in crystallization behaviour. We found that CuCl₂[Terpy-3CN] was not only able to form an stable crystallization-free gel but also was not able to crystallize in lower gelator concentration in any of solution observed over the course of a few months. So, our efforts for obtaining a suitable crystal of CuCl₂[Terpy-3CN] were inconclusive. In order to examine the effect of the solubility on the formation of single crystals of CuCl₂[Terpy-3CN], different pure and protic/aprotic mixed solvents with various ratios have been used as the growth media. As no crystallization process observed in any of cases, it can be concluded that for CuCl₂[Terpy-3CN], the interaction of gelator and solvent doesn't play a critical role in the 3D formation of crystals. Crystallization of a gelator complex system is normally a difficult task,

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although it is hard to obtain suitable crystal from terpyridine base complexes, dipyrazinepyridine base complex readily forms single crystals upon resolving in MeOH and subsequently cools to room temperature within a few minutes.

Crystal Structure. Using X-ray crystallography analysis, we obtained a deeper understanding of the nature of intermolecular interactions in the gel-phase aggregation by determining single crystals of these complexes. A helpful starting point in order to understand the likely supramolecular arrangements and the way they are likely to influence molecular aggregation in gel formation could be the study of crystal structures^{23,34}. We hypothesized that the gel formation may be similar to self-assembly processes in crystallization, at least in one-direction to formation of fibers⁶⁰. Interestingly, different crystal forms of CuCl₂[Terpy-4CN] are obtained from different solvents. We report here two structures for the polymorphs of this complex obtained from MeOH, Form I, a mixture of water and MeOH, Form II, the structure for the complex of CuCl₂[Dipyz-py-3CN] and CuCl₂[Dipyz-py-4CN], which were characterized by single-crystal X-ray diffraction. As shown in Figure 3, the coordination environment around the metal centers in all complexes is identical and can be defined in 1:1 metal to ligand complex. A distorted square pyramidal geometry can be best considered for defining of coordination geometry around each Cu atom. The five coordination sites of Cu(II) ion, are occupied by three nitrogen atoms of pincer-type ligand and two chloride ions. Despite the similarities in conformation of each related homologous terpyridine/Dipyrazinepyridine ligands, the 3D formation of each compound is surprisingly varied. Extended packing schemes are summarized in Figure S1. The packings are highlighted by a number of interactions. Some are relatively strong non-classical hydrogen bonds (C-H···N-C) and some are weak non-classical hydrogen bonds (C-H···Cl), Table S2, and moderately weak intermolecular slipped π - π stacking interactions ($C_{phen} \cdots C_{phen}$ and $C_{phen} \cdots C_{pyr}$),

Table S3. Apart from the strong and weak bonds that were discussed above, as a matter of fact, there are multiple very weak ones too.

Supramolecular Synthons. The correlate between the packing similarity of Low Molecular Weight Gelators (LMWGs) in the gel state as well as in the crystalline state^{23,62,63} has been discussed repeatedly in the literature. Clear evidence has shown that an ordered fibrous matrix is formed by Low Molecular Weight Gelator. The ordered 1D fibers resulted from the assembly of molecules through directional and strong intermolecular interactions⁶⁴. It must be noted that forming of ordered fibrous must be done in priority to crystallization moieties. It must be noted that regardless of the presence of self-willed structures of a fibrous matrix in the gel state, the deduction drawn from crystal states must be handled somehow cautiously. The presence of the mentioned anisotropic interactions are necessary for extending in only one direction through the crystal most likely leading to fast growth in only one direction and the fibers' growth.

The relative lack of such contacts in the other two dimensions barricades sidelong growth and thus crystallization. So, additional attempts have focused on clarifying the correlation between supramolecular aggregation patterns of a molecule in single-crystalline form and its gelling behaviour^{62,65,66}. Understanding the correlation between gelation and crystallization processes is obligatory to furnish rational approaches to the design of non-covalent, self-assembling gel soft matters. Thus, finding the rational design of relevant gel states have been challenging due to the particular correlation between self-assembly into either crystalline or fibril states²⁷.

In order to investigate the property-structure relationships, the inspecting of the supramolecular synthons in the crystal structures of the gelator is very important. Since recognition of intermolecular interactions is a key factor to correlate molecular structure and crystal packing, crystal engineering attempted to identify robust and repeatable supramolecular synthons.

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Repetition of synthons actually occurs in molecules that have the same chemical skeleton with different functional groups⁶⁷⁻⁶⁹. In fact, synthon repetivity shows specific robust synthons in related compound series.

All associations in the first instance through the formation of hydrogen bonding extended linearly and infinitely a one dimensional (1D) line. Close inspection of the crystal structures of Cu(II) complexes of this pincer ligands revealed that, pincer complexes assemble to form an infinite one dimensional (1D) array, which are held together by three kinds of interaction: (1) the hydrogen bonding between nitrogen atoms of cyano group and hydrogen atoms of the pyridine rings of neighbouring molecule (2) intermolecular C-H···Cl hydrogen-bonding interactions (3) π - π stacking interactions between phenyl ring and the other rings in the nearest adjacent complex. These three kinds of interactions are robust enough to order the assembled units into linear fiber-type aggregates. It might worth to notice that notwithstanding the presentment of an intercalary hydrogen bonding functionality (N_{pvrazine}) in the dipyrazinepyridine counterpart of terpyridine ligands, the one-dimensional synthon stayed intact; which led to the formation of the 1D chain along the main direction of the molecule. However, the additional electron withdrawing nitrogen atoms participated in hydrogen bonding and engaged in connecting the two neighbouring 1D chains, resulting in an overall 3D network, Figure 4. It indicates that these interactions may play crucial roles during the formation of the gel.

The control of the self-assembling mode at the molecular level must be considered as a key factor in the rational design of LMWGs. For the efficient growth of fibers, one-dimensional assembly is necessary, so, strong and highly directional self-assembling groups are selected. All of these interactions have the same orientation with the main direction of the molecule. In the case of pincer terpyridine ligands there aren't any functional group in the perpendicular

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orientation with the main direction of the molecule but in the dipyrazine-pyridine ligands the second nitrogen atoms in pyrazine ring have perpendicular orientation and play a vital role in the further linkage of the resulting chains to each other to form a 3D network. The interactions between the two chains are strong enough, which make it hard to further assemblies elongation in a one-dimensional way, and to generate extended fibers, resulting in the easy formation of the crystalline state. These witnessings are steadfast with the fibrillar contacts and interatomic separations promulgating 1D assembly whereas, in the crystalline state, molecules are aligned along multiple axes, allowing three-dimensional growth which has an impact on the using of crystal structures to specify supramolecular synthons for gelators. Syllogizing of interactions in the hydrogel fibrils by using crystal structure data must be done carefully. Mostly, packing arrangements between the gel and crystalline states are different. In hydrogelators studied herein, several factors suggest that although the packing modes are not identical but are similar. First, for all structures studied here, there is intramolecular hydrogen bonding robust enough to be repeated. Next, the diversity observed in both gel and crystalline state. So, it is presumed that the basic aggregation architecture is retained between the two states and that the crystals solely contain extra interactions that extend the growth of the 1D fibrils in 3D dimensions.

Morphological studies of the metallogels in different solvents. To better understand the gelation mechanism and get a deeper insight into the morphological features of metallogels with the respective solvents in the nanoscale dimension, SEM studies were carried out on their xerogels. To the understanding of the mechanism of gel formation, analyses of its structure are very important. The properties and behaviours of materials are rationalized by their structures. Study of structure-property correlation is a critical role of the gelator/solvent interaction and the fact that solvent polarity can significantly influence the morphologies. Solvent is incumbent for

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gelation to be objective. On the other hand, solvent has a critical role in the fine tuning of the molecular architecture during the self-assembling process as well as the self-aggregated properties of the resulted gel phase. Different morphologies in the gels can be tuned by the controlling the conditions, resulting in special properties of the supramolecular gels^{70,71}. Metallogels obtained from the different solvent were dried in a vacuum desiccator to give xerogels and then coated with gold and imaged by SEM, Figure 5. By simply changing the solvent in the case of CuCl₂[Terpy-3CN], the nanoscale morphology underwent a change from a large pores and plate like aggregates (water) to high pores network (10:1 MeOH: H_2O) to micro thin plate type morphology (10:2 EtOH: H_2O) to overlapping rugate layer structure for (10:3 PrOH: H₂O) and (10:3 IsoPrOH: H₂O) and densely packed fibrous morphology (10:3 Acetone: H₂O). The same results were obtained when the gelation behaviour of CuCl₂[Terpy-4CN] was tested, change in the solvent accompanied the similar morphological changes from a highdensity network of fibers (water) to branched networks (10:1 MeOH: H_2O) to overlapping rugate layer structure (10:2 EtOH: H_2O) to layer structure (10:3 PrOH: H_2O) to densely packed fibrous and layer structure (10:3 IsoPrOH: H₂O) and finally to 3D network resulted from bundles of fibers and large pores and plate like aggregates (10:3 Acetone: H_2O), Figure 5. These results clearly show the critical role of solvents in the final gel morphology. The gel resulted from the different solvent with different polarity was distinctly different morphology suggesting that the gel microstructure was very sensitive and the nature of the resulted fibrillar depends on the solvent used for the gelation as well as the gelator. A more scrupulously look at the competing gelator/solvent and gelator/gelator contacts show that the solvent can lead to substantial changes in both solubility and gelation ability. Significantly, when we focus on the crystal structure of two pseudopolymorphs of CuCl₂[Terpy-4CN], in molecular point of view the gelator/gelator

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interactions are similar, while solvent/gelator interactions are different. For these particular compounds, the difference in solvent/gelator interactions leads to fabricate different morphology of the gels. These results highlight the solvent role of in the gel morphology and crystal growth. Finding the two polymorphs resulted from terpyridine copper complexes not only supports our hypothesis about the mechanism of assembly but also confirms that variety in metallogels morphologies from different solvents actually originate from the same fiber aggregates. It means that for different solvent/gelator interactions, aggregated fibers could further aggregate together to form different morphologies.

The SEM studies in gel state show that tuning of the gel morphology can be done by the solvent combination. These results clearly show the delicate lines exist between insolubility, crystallization, gelation, and solubilization. The formation of fibers can be thought of as a consequence of inhibited crystallization or precipitation and, as such, may not represent the thermodynamic minimum, but rather a kinetically trapped structure. Furthermore, for kinetic reasons, thermodynamically unstable forms named metastable forms polymorphism in the crystal can be acquired. Since polymorph and gel state are both metastable forms⁷²⁻⁷⁵ maybe there is a relation between these two states. As a result, the crystal self-assembly and gel forming are essentially orthogonal or only very weakly coupled but observing any differences in polymorphism can increase the probability of diversity in gel morphology. There is a suggestion of the gelators being designed to imitate the 1D formation of crystal lattice and diversity in the crystal structure of a different polymorph, induces to obtain gels that have no similarities in term of their structures. A convenient way to alter the physical properties of a component that sustain crystal structures and gel morphology is controlling the process by which the self-assembly of the component is carried out to give the crystal or gel. This includes changing solubility by

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changing solvent, temperature and so one. Accordingly, the intermolecular interaction between the solvent and gelator is partly influenced as the gel stays maintained. However, the strength of these interactions influences the strength and morphology of the gel for the respective gelators as estimated by the lower T_{gel} values. Notice the difference in the network formation of the fibril structure is evident in the SEM. As other SEM images were carefully analyzed, we understood that not only the gelator but also the solvent used for the gelation plays an important role in the structure and the nature of the fibrillar networks.

Solvent-dependent UV-vis absorption spectra of CuCl₂[Terpy-nCN] complexes.

The UV-vis studies of the synthesized metallogelator were carried out in a series of solvents with 5 different polarities including H₂O, MeOH, EtOH, PrOH and isoPrOH, For CuCl₂[Terpy-3CN] in general the absorption spectra were not significantly changed by the solvent medium. As can be seen in Figure 6a, almost no shift in solvent-dependent UV-vis absorption spectra is found, this being explained due to the presence of similar solute-solvent interactions in various solvents used here. While in H₂O solvent a small red-shift is observed. The irregular red-shifted absorption peaks in H₂O related to those in other alcoholic solvents may be produced by increasing the dihedral angle between the fourth ring and terpyridine motif, which reduced the π conjugation. For CuCl₂[Terpy-4CN], Figure 6b, a correlation between λ_{max} and polarity of the solvent is observed. This can be mainly attributed to the fact that solvation by polar solvents leading to the generation of hydrogen bonding with water induced the solvated molecule to absorb at a lower wavelength compared to other solvents examined. This blue-shift shows relatively strong solute-solvent interaction between the water molecules and CuCl₂[Terpy-4CN] complex. The maximum absorption peak at 280 nm can be assigned to the intramolecular charge transfer state between the electron acceptor (cyano) group and the electron donor (terpyridine)

moiety, showed the solvent-dependency due to its strong hydrogen bonding. The weak absorption band resembling at 340 nm, which did not shift with increasing solvents polarity, was originated from π - π * transitions and it indicating that the formation of self-assembled aggregates by compound CuCl₂[Terpy-4CN] was cooperative. The self-assembled aggregates may be attributed to the synergistic operation of hydrogen bonding and π stacking interactions in the self-assembly aggregates of the compound.

Powder X-ray diffraction studies of CuCl₂[Terpy-4CN], and CuCl₂[Terpy-4CN].H₂O. Powder X-ray diffraction pattern of the xerogel of CuCl₂[Terpy-4CN], is recorded to achieve a better and deeper understanding regarding the self-assembly process, Figure 7. As it is clear from this Figure, no good fitting is observed between experimental PXRD patterns and simulated one from single crystal X-ray diffraction related to crystalline phase changes during the vacuum drying. It must be noted that since monitoring the formation of crystals under conditions favoring gelation was uncommon, the complex was dissolved in methanol and under slow evaporation to yield green block single crystals. In the PXRD pattern of the xerogel of CuCl₂[Terpy-4CN], only one big diffraction peak at $2\theta = 26.31^{\circ}$ was observed, which based on Bragg's equation corresponded to a *d*-spacing of 3.4 Å. These diffractions resulted from the corresponding π stacking interactions of pyridine rings of the ligand as well as π -Cl interactions between adjacent molecules in the chains. Figure 7(c) also shows the PXRD pattern of the xerogel of CuCl₂[Terpy-3CN]. As it is clear from this figure, similar to 4-cyano homologous, the presence of one big diffraction peak at $2\theta = 22.50^{\circ}$ and *d*-spacing of 3.9 Å shows the π -stacking interactions of pyridine rings of ligand.

Conclusion

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In conclusion, we have presented a simple terpyridine ligand decorated with the cyano substituent that leads to metallosupramolecular gels in aqueous media. To show the driving forces for the self-assembling of the metallogelators, their crystal structures have been scrutinized. The gelation mechanism involves the formation of one-dimensional (1D) nanofibrils in a straight line that is unlimitedly continued. In the next step, dipyrazine-pyridine counterparts were synthesized in an attempt to find a design strategy for gelators. All of the synthesized dipyrazine-pyridine compounds were either too soluble or crystalline in a wide range of solvent, and we were unable to access the gel state by them. What this observation has an effect on is mainly the determination of supramolecular synthons for gelator.

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SUPPORTING INFORMATION

Electronic Supplementary Information (ESI) available: The packing diagrams, hydrogen bonding and $\pi...\pi$ interaction data and X-ray crystallographic files in CIF format for structural determination of CuCl₂[Terpy-4CN], (CCDC No. 1510958), CuCl₂[Terpy-4CN].H₂O, (CCDC No. 1510957), CuCl₂[Dipyz-py-4CN].H₂O, (CCDC No. 1510959), and CuCl₂[Dipyz-py-3CN] (CCDC No. 1511109). This material is free of charge *via* Internet at http://pubs.acs.org.

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Y	Formula	X	Y	Ζ	Gel	Crystal
Z	CuCl ₂ [Terpy-3CN]	СН	Н	CN	~	×
	CuCl ₂ [Terpy-4CN]	СН	CN	Н	~	✓
X	CuCl ₂ [Dipyz-py-3CN]	Ν	Н	CN	×	✓
	CuCl ₂ [Dipyz-py-4CN]	N	CN	Н	×	\checkmark

Scheme 1. Molecular structures of synthesized complexes.

Solvent	CuCl ₂ [Terpy-3CN]			CuCl ₂ [Terpy-4CN]			
	Phase	MGC(mg mL ⁻¹)	T _{gel}	Phase	MGC(mg mL ⁻¹)	T _{gel}	
H ₂ O	G	0.93	90	G	1.15	95	
МеОН	S	-	-	S	-	-	
EtOH	S	-	-	pS	-	-	
PrOH	pS	-	-	pS	-	-	
IsoPrOH	pS	-	-	pS	-	-	
BuOH	Ι	-	-	Ι	-	-	
Aceton	S	-	-	S	-	-	
n-hexane	Ι	-	-	Ι	-	-	
CH ₂ Cl ₂	S	-	-	pS	-		
MeOH:H ₂ O	G	2.53	69	G	2.84	75	
EtOH:H ₂ O	G	1.83	73	G	2.15	68	
PrOH:H ₂ O	G	1.45	84	G	1.68	85	
IsoPrOH:H ₂ O	G	1.29	81	G	1.74	87	
Aceton: H ₂ O	G	0.98	73	G	1.25	80	

 Table 1: Gelation properties of CuCl₂[Terpy-3CN] and CuCl₂[Terpy-4CN]

G: gel; S: solution; pS: partly soluble; I: insoluble





Figure 1. Synthesis of CuCl₂[Terpy-nCN], metal complexes and formation of corresponding copperohydrogels.



Figure 2. Plot of T_{gel} (gel-sol transition temperature) versus gelators concentration at different solvent.

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(d)

Figure 3. ORTEP view of the crystal structure of CuCl₂[Terpy-4CN], (a), CuCl₂[Terpy-4CN].H₂O, (b), CuCl₂[Dipyz-py-4CN].H₂O, (c), and CuCl₂[Dipyz-py-3CN], (d), showing distorted square-based pyramid N₃Cl₂ coordination environment around metal centre. Thermal ellipsoids are shown in 30% probability level. Selected bond distances (Å) and angles (°): Cu1-N1=2.073(7), Cu1-N2=1.947(7), Cu1-N3=2.053(7), Cu1-Cl1=2.225(3), Cu1-Cl2=2.427(3), N1-Cu1-N3=156.6(3), N2-Cu1-Cl1=150.9(3), N1-Cu1-Cl2=97.5(2), Cl1-Cu1-Cl2=108.4(1), for CuCl₂[Terpy-4CN], Cu1-N1=2.088(9), Cu1-N2=1.942(9), Cu1-N3=2.134(9), Cu1-Cl1=2.218(2), Cu1-Cl2=2.566(4), N1-Cu1-N3=154.6(4), N2-Cu1-Cl1=163.2(3), N1-Cu1-Cl2=92.7(3), Cl1-Cu1-Cl2=103.0(1), for CuCl₂[Terpy-4CN].H₂O, Cu1-N1=2.027(5), Cu1-N3=1.984(4), Cu1-N4=2.029(5), Cu1-Cl1=2.229(1), Cu1-Cl2=2.408(2), N1-Cu1-N4=157.5(2), N3-Cu1-Cl1=146.9(1), N1-Cu1-Cl2=95.5(1), Cl1-Cu1-Cl2=110.6(1), for CuCl₂[Dipyz-py-4CN].H₂O and Cu1-N1=2.08(1), Cu1-N3=1.955(7), Cu1-N4=2.06(1), Cu1-Cl1=2.238(3), Cu1-Cl2=2.441(4), Cu2-N7=2.024(8), Cu2-N9=1.96(1), Cu2-N10=2.03(1), Cu2-Cl3=2.218(3), Cu2-Cl4=2.458(4), N1-Cu1-N4=155.3(4), N3-Cu1-Cl1=156.0(3), N1-Cu1-Cl2=93.4(3), Cl1-Cu1-Cl2=100.9(1), N7-Cu2-N10=155.4(4), N9-Cu2-Cl3=153.5(3), N7-Cu2-Cl4=99.6(3), Cl3-Cu2-Cl4=114.4(1) for CuCl₂[Dipyz-py-3CN].



adduct from formation of 3D network.





Figure 5. SEM images of xerogels from $CuCl_2[Terpy-3CN]$ (a) in water, (b) in 10:1 MeOH: H_2O , (c) 10:2 EtOH: H_2O , (d) 10:3 PrOH: H_2O , (e) 10:3 IsoPrOH: H_2O , (f)10:3 Acetone: H_2O and $CuCl_2[Terpy-4CN]$ (g) in water, (h) in 10:1 MeOH: H_2O , (i) 10:2 EtOH: H_2O , (g) 10:3 PrOH: H_2O , (k) 10:3 IsoPrOH: H_2O , (l)10:3 Acetone: H_2O .





Figure 6. Solvent-dependent UV-vis absorption spectra of CuCl₂[Terpy-3CN], (a), and CuCl₂[Terpy-4CN], (b), complexes in different solvents including H₂O, MeOH, EtOH, PrOH and isoPrOH.



Figure 7. Simulated PXRD pattern generated from the CIF file of single crystal analysis of CuCl₂[Terpy-4CN] (a), and of CuCl₂[Terpy-4CN].H₂O, (b), and experimental powder X-ray diffraction (PXRD) pattern of the of CuCl₂[Terpy-4CN].H₂O powder, (c), xerogels of CuCl₂[Terpy-4CN], (d), and of CuCl₂[Terpy-3CN], (e). For generation of simulated pattern FWHM factor is considered equal to 0.5.

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Are Gelation behaviour Predictable through Crystal Engineering Approach? A Case Study in Four Similar Coordination Compounds

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In the present paper, a detailed study on the gelating properties of a series of terpyridine and dipyrazine-pyridine ligands, [Terpy-nCN] and [Dipyz-py-4CN], in the presence of CuCl₂ salt have been reported. Gelation and crystallization behaviuor of the resulted complexes indicate that the gelation and crystallization of the present molecular system is derived from the subtle balance of molecular shape and intermolecular interactions. These results have provided an insight into the balance between the solution, gelation and crystallization with subtle molecular variations.

